THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

THE EIGHTY-EIGHTH GENERAL MEETING of the Institution was held at the Royal Society of Arts, John Street, Adelphi, on Tuesday, November 10th, 1925, Sir Thomas Holland (President) occupying the chair.

The Secretary read the names of members elected, and transferences made, since the last meeting, as follows :—

Members.—Harry Yule Vivian Jackson, Joseph Stanley Jackson, and Rochfort Henry Sperling.

Transferred to Member.—Daniel Alfred Hart.

Associate Members.—John Edward Ford, John Nicholson Hazeldon, Vladimir U. Hodosh, and Gilbert Stanley Hodson.

Transferred to Associate Member.—Charles Alexander Moon.

Students.—Christian William Breukelman, William Watson Connor, Michael Eugene Adrian Iaroslavici, Alister Michael Nicholas, Robert Ernest Palmer, and Albert Thomas White.

Associates.—Austin Lloyd.

Members were also reminded that nominations for Council must be in the hands of the Secretary by January 31st, 1926.

The President said that Mr. Ashley Carter, who had been the Institution's delegate at the International Drilling Congress at Bucharest, had just returned, and had kindly consented to give the meeting a short account of the proceedings of the Congress before the papers which were to be presented were read.

Mr. Ashley Carter said he was appointed by the Institution, at the invitation of the International Drilling Congress, which had just been held at Bucharest, to represent it there. About 350 people were present at the opening of the Conference, and meetings were held for five days, during which twenty-one papers were either read and discussed or presented. There was not sufficient time to read them all. Concurrently with the Congress an exhibition was held, and the exhibition itself was very interesting. Many manufacturers were represented there. He thought probably the German manufacturers dominated the exhibition, but the

exhibits themselves were really of high merit. Following the exhibition, a series of visits were arranged to various oilfields, refineries and mining districts, all of which were very interesting, particularly owing to the fact that at the present time there was very great activity in Rumania, chiefly for the reason that a deeper sand had recently been discovered in the Moreni field, which was resulting in a tremendous amount of activity in drilling. Again, there was the Ceptura field, which was likely to be very active during the next few months.

There were many drilling systems in use in Rumania, but he thought it could safely be said that the rotary was steadily forging ahead, and the probability was that this would be the system which would dominate the drilling in that country. There had been a very large increase recently in the production of oil, and the whole industry at the present time was in a very flourishing condition.

In conclusion, he wished to acknowledge the kindness and hospitality which, as a delegate of the Institution, he had received in Rumania.

The following paper was then summarised, in the absence of the author, by Dr. A. E. Dunstan :—

The Principles of High Vacuum Distillation of Mineral Oils.

By Leo Steinschneider.

In the year 1912, a lecture by the author before the Eighth International Congress of Applied Chemistry, at the Columbia University in New York, on the favourable results achieved in the high vacuum distillation of petroleum, met with little more than academic interest.

Working under greatly reduced pressure was at that time still wholly unknown in the petroleum industry of the United States. In Europe the first installations were already in operation. There were many opponents, and it was only slowly, step by step, that they were convinced. Meanwhile some 250 vacuum stills were put to work for the manufacture of lubricating oils from all kinds of crude oil in various parts of the world, and now nearly all the large refineries in Europe have introduced high vacuum plant, also many oversea refineries, e.g., in India, the Dutch East Indies, Venezuela, etc.

Probably no other system of distillation has won such rapid and widespread popularity. The large refineries of the United States have also adopted this process. This was done during the war, the State institutions which were at that time entrusted

with the investigation of the most efficient refining methods having proved beyond doubt the great value of distillation under vacuum.

Recently, during a long tour of inspection of refineries in the United States, the author was able to ascertain that the largest oil companies in that country produce their lubricating oil distillates by the high vacuum method.

Among other plant which was seen at work in one Californian refinery alone were 74 vacuum stills, and there is scarcely any large oil company which will not now occupy itself with the question of the early introduction of high vacuum.

A paper on the principles of high vacuum distillation will therefore doubtless be of interest to many connected with the petroleum industry.

It is well known to every practical oil man that the distillation of petroleum is always accompanied by partial decomposition; this is less when the lower boiling constituents are being distilled off; it increases, all other conditions being equal, in the measure that the boiling point rises.

Provided that the plant used is good and appropriate for the purpose, this circumstance does not practically affect the result of the distillation to any great extent so long as the distillation temperature does not appreciably exceed 300°–320° C. At this temperature, however, decomposition begins to manifest itself in an increasing degree, no matter what the origin of the raw material; and every means must be employed to diminish the influence of the decomposition, in order to avoid distillation losses and to obtain good lubricating oils, a point with which I will now deal.

Although the distillates up to a boiling point of about 300° C. are not affected by the unavoidable decomposition, this does not apply to the residuum, which forms the raw material for lubricating oil distillates. In the distillation of the light products also—naphtha, kerosene and gas oil—decomposition must be avoided as far as possible if the residuum is to be further treated advantageously for the production of lubricating oils.

The objects of lubricating oil distillation are the production of distillates with good physical properties, whilst avoiding distillation and refining losses, and the manufacture of an asphalt, which is as far as feasible free from coke even at the highest melting points. The best distillation can only avoid the formation of free carbon, it cannot remove the coke already present in the raw material. The asphalt (bottoms) obtained as a residuum from the oil distillation will therefore always contain at least the percentage of coke present in the raw material from which it is won.

The aforementioned and known occurrence—that at about 320° C. greater decomposition (cracking) sets in, and this notwith-

standing the nature of the distillates obtained—necessitates the lowering of the boiling point as near as possible to (and preferably below) this, in a certain sense, critical temperature. There is only one known means of attaining this object, and that is diminution of the absolute pressure, or, in other words, distillation under vacuum. This can be achieved in two ways: either by injecting steam into the liquid or by diminishing the pressure in the condensing equipment; further, by the simultaneous employment of both means, that is, by diminishing the absolute pressure in the condensing equipment and at the same time injecting steam into the liquid to be distilled.

The purpose of the steam is, primarily, to lower the temperature by diminishing the tension of the oil vapours, and it is therefore, like the air pump, a means of reducing the pressure, although the physical procedure is different. This is demonstrated in "Die wissenschaftlichen Grundlagen der Erdoelindustrie," by Dr. Leo Gurwitsch, and from it some of the data given later are taken.

It is only secondarily that the steam is used for the purpose of bringing about an active circulation of the liquid, in order to avoid local overheating.

Two factors, however, set a certain limit to the utilisation of steam. On the one hand, too large a volume of steam adversely affects economy in working and, on the other hand, results in lowering the quality of the distillates because, due to the emergency of very large quantities of steam from the evaporating surface, considerable quantities of undistilled liquid particles are mechanically carried over into the distillates, which render the subsequent chemical treatment much more difficult and expensive and are thus the cause of large losses and impaired qualities. The percentage of particles carried over mechanically can, of course, be reduced by liquid separators, but never wholly eliminated when the same has gone beyond a certain stage. Reduction of the distillation capacity naturally affords a remedy, but this results in inadequate utilisation of the plant.

According to Gurwitsch there exists between the physical factors, in the distillation of oil with steam under the absolute pressure P, the following connection:—

$$(1)\quad p = P\frac{18}{18 + a\,M}$$

In this equation

p signifies the vapour tension of the oil corresponding to the temperature T;

P the absolute pressure bearing on the surface;

M the molecular weight of the oil, which may be assumed as roundly 400;

a the quantity of steam used to one part of distilled oil;

18 the molecular weight of the water.

We will now assume that the heaviest fraction would evaporate under atmospheric pressure at 500° C., which is approximately the case with heavy cylinder oil, and that at normal atmospheric pressure an evaporation temperature of 320° C. is not to be exceeded. In accordance with the accompanying diagram the oil must then be distilled off under a partial pressure of 20 m/m mercury, the quantity of steam required for each part distillate being:—

$$(2)\quad a=\frac{(P-p)\ 18}{M\ p}=\frac{(760-20)}{400\ \ 20}\ 18=1{\cdot}65$$

Therefore, in order to attain this, theoretically 1·65 parts steam are necessary for 1 part oil distillate.

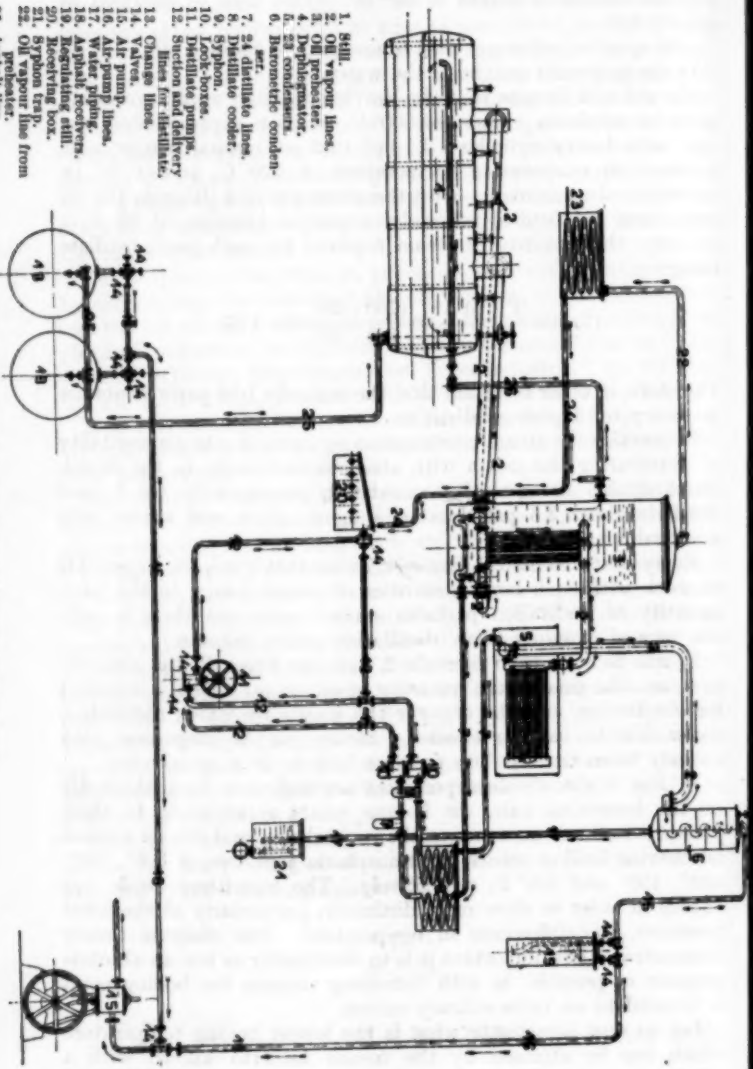
In practice the steam consumption is, owing to the impossibility of distributing the steam with absolute uniformity in the liquid, about double the quantity calculated, consequently for 1 part distillate about 3·5 parts water, a figure which well agrees with practical tests.

Every practical man is, however, aware that it is quite impossible to work with such large quantities of steam, owing to the large quantity of undistilled particles carried over, and there is only one way of avoiding this: distillation under vacuum.

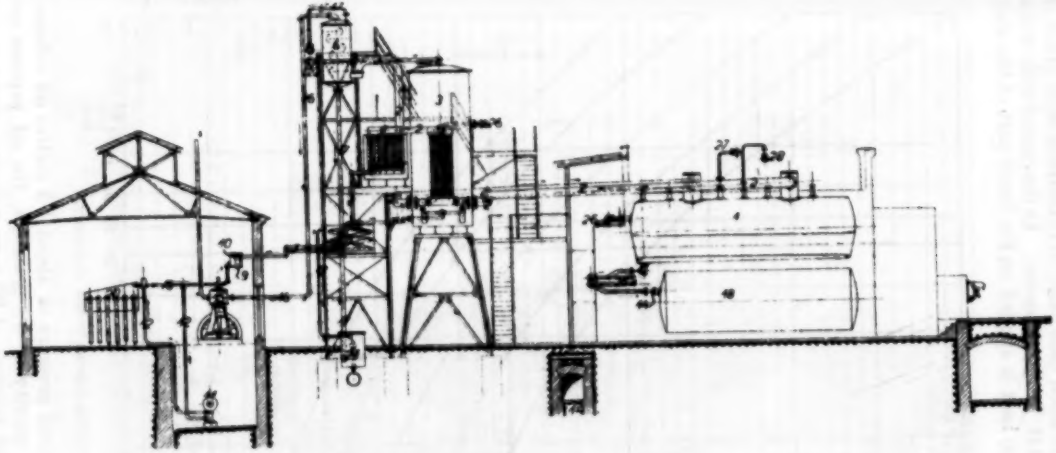
It will be seen from formula 2 that the lower P, the absolute pressure, the smaller the quantity of steam (a) which is required for distillation, and the cheaper the means by which distillation under 320° C. can be effected. Steam can be dispensed with entirely when the absolute pressure falls to 20 m/m mercury.

In Fig. 1 the absolute pressures are indicated logarithmically on the horizontal axis, the boiling points appertaining to these pressures in linear measures on the vertical axis, and this for various oils having boiling points, at atmospheric pressures, of 300°, 350°, 400°, 450° and 500° C. respectively. The logarithmic scale was chosen in order to show more distinctly, particularly at the lower pressures, the differences in temperature. This diagram clearly demonstrates how important it is to work under as low an absolute pressure as possible, as with increasing vacuum the boiling point is lowered to an extraordinary extent.

Let us now investigate what is the lowest boiling temperature which can be attained by the means hitherto known with a distillate which under atmospheric pressure would boil at 500° C.



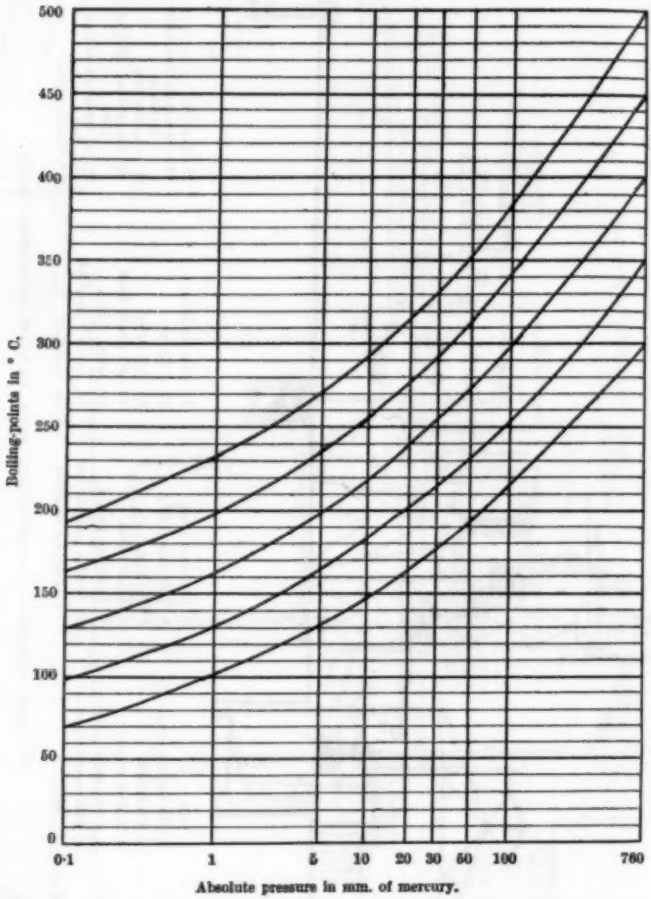
OUTLINE OF HIGH VACUUM PLANT WITH PREHEATER.



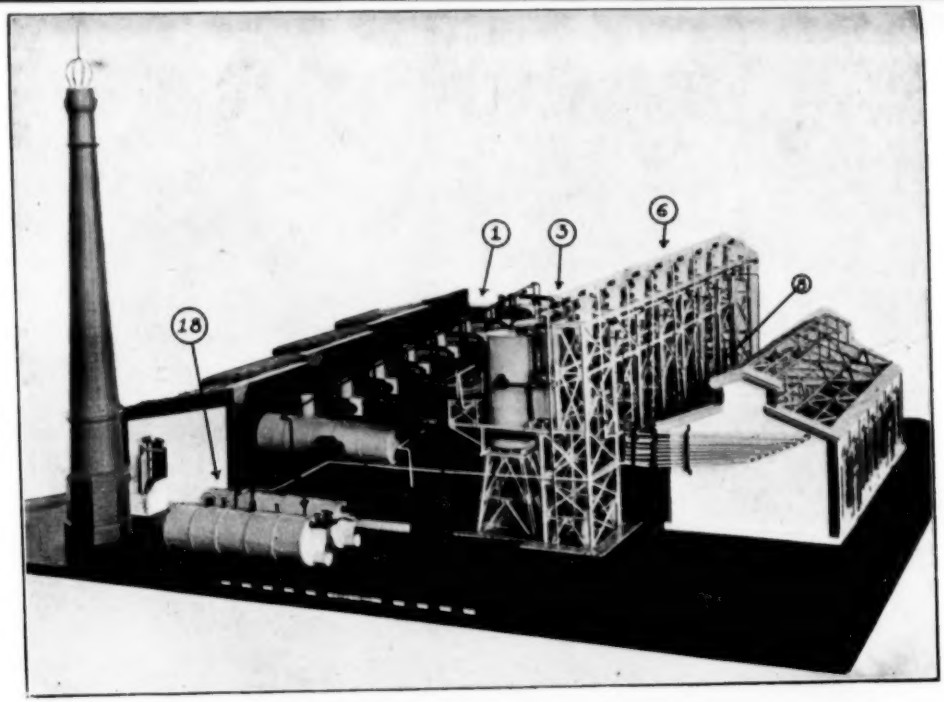
1. Still.
2. Oil vapour lines.
3. Preheater.
4. Dephlegmator.
5. Condenser.
6. Barometric condenser.
7. Distillate lines.
8. Distillate cooler.
9. Syphon.
10. Look boxes.
11. Distillate pumps.
12. Suction and delivery lines for distillate.
13. Change lines.
14. Valves.
15. Air pump.
16. Air pump lines.
17. Water pipes.
18. Asphalt receivers.
20. Tail box.
21. Syphon.
22. Oil vapour line from preheater.
25. Asphalt line.
26. Continuous oil-feed line.
27. Intermittent oil-feed line.
28. Steam pipes.

CROSS SECTION OF CONTINUOUS HIGH VACUUM DISTILLING PLANT.

Heating and evaporation take place in cylindrical stills of 2·6—3 metres (8 ft. 6 in.—9 ft. 10 in.) diameter. In the case of stills which have no internal flue, heat is applied on the lower part of the shell,

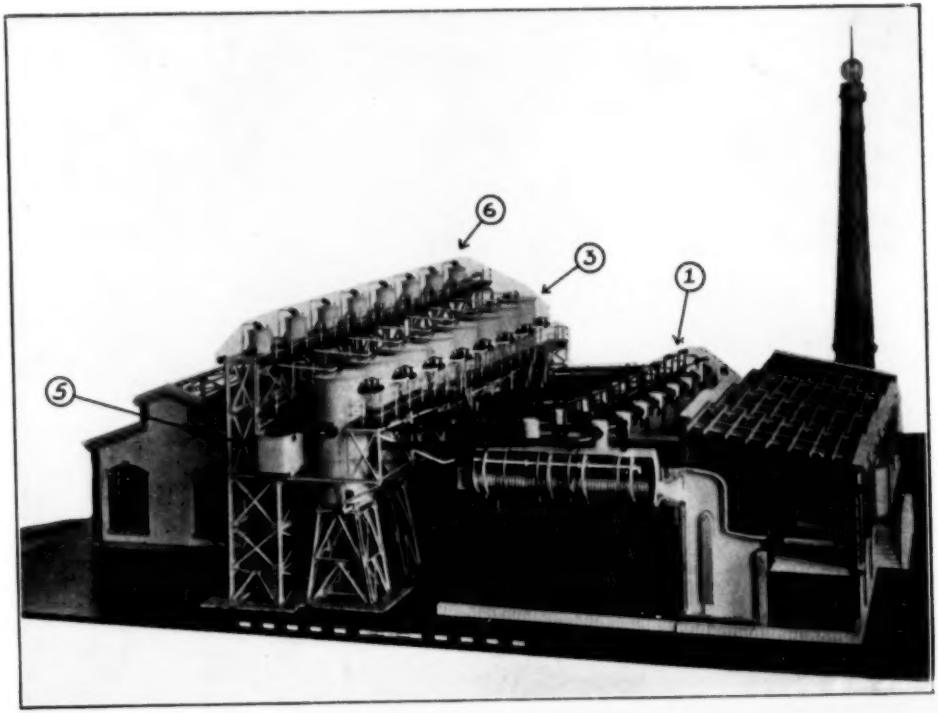


therefore under a liquid pressure of about 1·5 metres oil column. Assuming a specific gravity of 0·8 grammes, the oil vapours are formed under a liquid pressure of 90 m/m mercury, consequently altogether 115 m/m if the absolute pressure in the vapour space



MODEL HIGH VACUUM DISTILLING PLANT.

For references see figure on p. 519.



MODEL HIGH VACUUM DISTILLING PLANT.

is 25 m/m. The temperature measured in the vapour space corresponds to the vacuum existing therein as shown by the vacuum meter, because the steam particles on their way to the surface of the liquid are expanded to the absolute pressure of the vapour space. The formation of the oil vapour, however, takes place under the increased pressure of 115 m/m and therefore at a boiling temperature corresponding to this pressure. Although the unfavourable influence of the high liquid layer is somewhat mitigated by the circumstance that evaporation occurs not only at the lowest part of the shell, but also at parts of the same at a higher level, and further, also in consequence of the natural circulation of the liquid, it remains nevertheless unquestionable that a considerable portion of the vapour bubbles are formed under the full effect of the high liquid layer, therefore under conditions where decomposition is inevitable unless steam is applied.

In stills with internal flue the effective heating surface is about 800 m/m higher towards the surface of the liquid, so that the liquid pressure exerted on the vapour bubbles formed is reduced to about 0·7 M. oil column, which corresponds to a mercury column of approximately 45 m/m. The oil bubbles are therefore under a total pressure of only 70 m/m, if the absolute pressure in the vapour space is, as previously assumed, 25 m/m. An internal flued still must therefore always give more favourable results than an ordinary, externally fired, cylindrical still.

In both cases, however, as shown by the diagram, it is necessary to use steam, as in each case a reduction of the boiling point below 320° C. cannot be attained, even if it were possible to reduce the absolute pressure in the vapour space to zero.

The height of the vacuum attainable in the vapour space of the still depends, when distilling with steam, solely upon the temperature of the cooling water available for condensing purposes. This is (with 25° C. fresh cooling water and assuming 10° temperature increase to 35° C.) 45 m/m mercury. Under very favourable cooling water conditions an absolute pressure of about 20 m/m can be attained.

The inordinately growing diminution, especially in the realm of the lowest pressures, and the reduction hereby possible of the quantity of steam, and in certain circumstances its complete elimination (see formula 2) have in America led to efforts being made to reduce the absolute pressure to the fullest extent which technical means allow. Plant of this description, distilling under absolute pressures of 5—25 m/m, without the application of steam, is in operation and giving satisfactory results. In such plant the oil is distilled in cylindrical stills, without internal flue, and having a diameter of about 2·9 metres and

a length of about 10 M. (about 9 ft. 6 in. by 32 ft. 10 in.); the distillates, which are only treated with alkali, are also redistilled under high vacuum, and then yield without further chemical treatment marketable products possessing very good physical characteristics. The extent to which the dual distillation affects the profitableness of this method of working would have to be investigated in each individual instance. With suitable improvements in the equipment necessary for the purpose, particularly in the still imperfect dephlegmation, a considerable advance in this direction may be anticipated in the near future.

In a further paper it is hoped to deal at length with novel developments, so soon as practical results are available from plant embodying new principles. This plant is at the present time under construction.

The new endeavours confirm the correctness of the following old principles:—

(*a*) Distillation under as high a vacuum as can be attained with known means, without making undue demands upon the operators of the plant.

(*b*) Eliminating or minimising to the utmost the use of steam.

(*c*) Active circulation of the liquid, in order to prevent even partial cracking when not using steam or only minimum quantities of steam.

(*d*) Avoidance of redistillation as far as possible; by the use of modified dephlegmating devices.

(*e*) Safety in operation, also when distilling the heaviest oils, without risk of the burning through of the heating surfaces.

(*f*) Avoidance as far as possible of subsequent chemical treatment of the distillates.

Preliminary tests with the new plant warrant the expectation of complete success.

And now a few particulars—collected during an experience of upwards of fifteen years—regarding the favourable results already obtained.

The principal value of high vacuum distillation consists in that it is precisely the inferior, heavy asphaltic oils (the conversion of which into heavy lubricating oils was unprofitable and frequently impossible), which are the most advantageous for high vacuum distillation, as all the fractions, even the heaviest cylinder oils, are won as distillate (overhead distillates) and not as residuum (bottoms). Only the asphalt—a superior coke-free material—remains in the still.

Paraffinoid oils can also be distilled with equal advantage, as the distillates won, owing to there being practically no decomposition during distillation, contain the paraffin in amorphous state. They can therefore be centrifuged without difficulty, and then yield lubricating oils having a high cold test. As far as present technical knowledge goes, the future in this domain would appear to belong to the centrifugal, but it is expressly emphasised that oils containing crystalline paraffin, as won in ordinary distilling plant, cannot be deparaffined by centrifugal apparatus.

As compared with distillation without vacuum, the advantages of high vacuum distillation may be summarised as follow:—

Economy in fuel oil consumption, about 50 per cent.
Extra yield in distilling, about 4 per cent.
Extra yield in refining, about 4—6 per cent.
Saving of sulphuric acid, 50—75 per cent.

It has been proved beyond question that in every instance all products possess better physical properties; safety in operation is greater, as, due to the vacuum, leakages cannot occur; repairs are practically never necessary.

In every instance these advantages have covered the total capital outlay in less than one year. High vacuum plant will soon not be found missing in the modern refinery.

In conclusion, the author's thanks are due to Dr. A. E. Dunstan for the willingness with which he undertook to read this paper, a kindness which has enabled me—prevented from reading it personally by pressing business affairs—to respond to the invitation with which the Institution of Petroleum Technologists has honoured me and to place my views before its members.

DISCUSSION.

The President said he would convey the thanks of the Institution to Dr. Steinschneider for his description of the process dealt with in the paper, and to Dr. Dunstan for kindly summarising its contents. The process was already known and had been described elsewhere, but the Institution was glad to have an authoritative account of the high vacuum distillation process to put on record in its Transactions.

Dr. W. R. Ormandy said it was a somewhat extraordinary tribute to the oil industry that a process which in practically all its details—certainly its theory—has been known for fifty years, and which had been applied on a very large scale to the distillation of an oil-like substance which decomposed at 300° C., i.e.,

glycerine, for at any rate thirty years, should now be presented as if it were something new.

Mr. A. A. Ashworth said the paper did not give the actual amount of fuel used in the system described as run with steam, such as was generally used on the Continent, but in one or two instances in which he saw the system he found that an inordinate amount of fuel was still used—up to 30 per cent. of the through-put in one case. In that case the people concerned were distilling off about 70 per cent. of the raw oil, and they were using 1·8 kg. of steam to each 1 kg. of oil. Under those conditions, of course one must expect a very heavy fuel consumption, but a system which possibly might, under ordinary usage, use 20 per cent. of fuel was still uneconomical, considering that the theoretical amount of heat necessary to distil oil would probably be in the neighbourhood of somewhere under 2 per cent. of the through-put. The extra heat, of course, was mainly used in the making of the steam, though that was an idle use of the fuel so far as the distillation was concerned. It was also lost in the stack gases, because the distillation had to take place for a long time at a high temperature. In the instance which he had quoted there was a considerable amount of cracking which took place even under the conditions quoted. Probably an equal amount of oil was cracked to the amount of heavy oil distilled over, and that was probably due to the long time during which it was necessary to keep these oils at a high temperature.

He would like some information as to the actual amount of fuel used in the new systems to which Dr. Steinschneider referred. He had seen references to the Schultze system, but so far as he knew no details had ever been published.

Mr. E. C. Craven said that in connection with the equation of Gurwitsch, it was stated in the paper as something which merely rested on the authority of Dr. Gurwitsch. He thought, however, it could be obtained very easily. When one had two liquids which were indifferent to each other, and there was no chemical action between the vapours formed, the total pressure P was equal to the partial pressure of the oil plus the partial pressure of the diluent vapour, which in the present case was water.

From Avogadro's law the volume of each vapour present would be proportional to its mass and inversely proportional to its molecular weight, and the partial pressures of the vapours were proportional to their volumes. One could, therefore, write

$$P = p_{oil} + P_{H_2O} = \text{const.}\ (1/M + a/18)$$

Where a=weight of water present to 1 part of oil

$$\therefore \quad p_{oil} = P.\frac{1/M}{1/M+a/18}$$

$$= P\,\frac{18}{18+aM}$$

That was Dr. Leo Gurwitsch's equation.

Later on in the paper there was a statement to which some exception could be taken. It was said that in a particular still heated at the bottom, owing to the hydrostatic pressure of the liquid above the bottom of the still, even if one could reduce the absolute pressure in the still to zero, one would not get any distillation by 320° C. That sounded very doubtful. There were the layers of oil in contact with the bottom of the still, which he thought would superheat a few degrees; they would diminish in density and be carried by convection towards the top of the still, and the pressure becoming lower, burst into gas there. That supposed there were nuclei round which the bubbles could form. The major factor was probably the provision of nuclei for the formation of the bubbles. The excess pressure was $2\frac{T}{R}$, where R was the radius of the bubble and T the surface tension. If the radius were very small, the excess pressure could be very large. In a very clean vessel the bottom layers of oil would have to be super-heated considerably before one would get vapour formation. The most important function of steam was to assist the boiling by providing bubble nuclei. If it were a matter of obtaining a low partial pressure of the oil and 760 mm. absolute pressure, he thought some inert gas, flue gas, for example, might be used and circulated instead of steam.

Dr. Paul Dvorkovitz mentioned that in 1884 the use of the vacuum process had been introduced in Baku, and one firm had been distilling all their lubricating oil by means of that process. So high a vacuum as that to which Dr. Steinschneider referred was not used, but it was quite a high vacuum, nevertheless. With that system, continuous distillation could be employed, whereas with a high vacuum he doubted if it would be possible to have continuous distillation. It was very seldom that the lubricating distillates obtained from the different crude oils require for their refining the same quantity of acid. For example, lubricating distillates from Romany (Baku) crude require much less acid than lubricating distillates from Bibi Eibat (Baku) crude, which is inferior, and contains a large quantity of unsaturated hydrocarbons, so that more acid had to be used. He believes that no further

economy can be achieved by the vacuum process, as at present only about one-half per cent. of sulphuric acid is used. The quantity of fuel was not more than 4 to 5 per cent., so he did not think there was much room for any reduction of the fuel.

Mr. W. H. Coleman, also referring to Dr. Ormandy's remarks, said vacuum distillation had been used in this country in connection with tar distillation for some twenty-seven to thirty years with very satisfactory results in preventing decomposition of the higher boiling oils and in reducing the fuel bill for distillation.

Mr. McConnell Sanders said it seemed to him that the paper came at a very opportune moment in view of the fact that in the country which was usually regarded as the motherland of the petroleum industry some startling claims had been made recently for the application of a particularly high vacuum without the use of steam. The apparatus to which he referred called for a special construction of still, a special arrangement of vacuum pumps, and—perhaps the most novel feature—a special arrangement for heating, for distributing the heat by a radiation furnace instead of the usual underfired system. The results claimed for the process were somewhat extraordinary. It had been stated that not only could lubricating oils be easily obtained as distillates, but that no sulphuric acid was required, and the products could be taken straight out of the still and sold in the market.

He had one comment to make on the latter statement, and that was that the qualities in respect of colour which made lubricating oils accepted by certain markets were not entirely sustained by the process in question; the oils went off colour somewhat rapidly. In comparing the results of the so-called extremely high vacuum with those obtained by moderate vacuum and properly regulated steam distillation, there did not seem to be a very great deal of difference. That was probably due to the limitations imposed in actual practice. It was very difficult to maintain high vacua, and it was also difficult to maintain on a large large scale a perfect distribution of heat, and disengagement of vapours, without the use of steam, though it could be easily done in the laboratory. Practical refiners certainly found a value for high vacuum processes, but they did not give them the exaggerated importance which was now being attached to them by people on the other side of the Atlantic, who had apparently forgotten that high vacuum distillation had been carried almost to its experimental limits on this side, in the vacuum of the cathode light.

Mr. B. C. Allibone said there was one aspect of vacuum distillation to which he would like to draw attention, and as it was

rather against the application of excessive vacuum in distillation, he spoke with a certain reserve, because it was only a single aspect, viz., the effect on the stability of the oil. As was well known in the case of cylinder, automobile and transformer oils, the stability was a factor of some importance, and it might be thought that by distilling any crude oil with an excessively high vacuum one would get a product which would not sludge in use. That, however, was not the case; everything depended on the original contents of the crude oil distilled. It was quite obvious that however good a distillation was used, one could not make the finished product any better than it was originally. The danger was that one might expect to get too good results from the high vacuum system. In his own experience he had distilled what might be called a medium quality crude oil, and obtained from it, by using a vacuum of four mm., a beautifully coloured oil of transformer oil consistency. That oil, when it came to a sludge test, proved worse than a corresponding oil prepared from the same base by the ordinary methods of distillation, using a tolerable vacuum and a fair amount of steam. The reason, he presumed, was that in the vacuum distillation one avoided decomposing substances which would be decomposed in the still by ordinary distillation, and all that happened was that those substances came over and were decomposed during the sludging test, or alternatively, the case quoted may be a phenomenon corresponding to the not unfrequent occurrence of an oil, which, after a heavy treatment with some agent such as charcoal or fuller's earth, gives a worse sludging value than before treatment. It was just the same with the heavy oils. So far as his experience went, to produce what might be described as a perfect cylinder oil, the cylinder oil base must conta in a large percentage of a C_nH_{2n-4} series of hydrocarbons of high molecular weight, and if these compounds were not in the original oil there was no chance of producing them in the finished product, or obtaining a super-heat steam cylinder oil of really good quality.

Dr. A. E. Dunstan, replying on behalf of the author, said that Dr. Steinschneider would have the discussion to deal with personally, and therefore he himself did not propose to deal with all the points raised. He would like to allude, however, to one or two which were of interest to him. Mr. Craven mentioned that Gurwitsch's equation could be readily demonstrated from first principles, and personally he thought Dr. Gurwitsch might have derived that equation in the way Mr. Craven had shown. With regard to Mr. Craven's other remarks, he thought the most important matter in effective steam distillation or gas distillation was the maintenance of proper equilibrium between the vapour and liquid phases. He

thought in the ordinary methods that equilibrium was not attained, and therefore a considerable amount of extra steam was required.

Referring to Dr. Ormandy's remarks, he thought the whole point Dr. Steinschneider made in his paper related to the use of a very high vacuum. Everyone knew that a moderate vacuum had been used for years past, but that was by no means the same thing. As far as he knew, there was no reference in the paper to any continuity of operation. Clearly and obviously, if distillation could be effected continuously there would be a vast improvement, because, apart from the question of difficulty of getting equilibrium there could be no doubt that many of the troubles that occurred in the manufacture of lubricating oil were due to the fact that heavy oil was kept stewing in the stills for 30 or 40 hours, during which period all kinds of reactions could take place. That was a matter of some importance,

The last speaker had made a very obvious point, that if one had not got a certain series of hydrocarbons in the crude oil, that series could not be produced afterwards, but he did not think that this was implied in the paper. All that Dr. Steinschneider claimed was that by using these very high vacua he was getting better results than were obtained from the same crude oil treated by ordinary processes.

Dr. Steinschneider subsequently replied in writing:—With reference to the remarks of Dr. Ormandy he would enlarge somewhat, as he desired to deal at the same time with questions which arose later on in the discussion.

It is a fact that distillation with vacuum has been long known in the chemical industry, and the manufacture of glycerine is a good illustration of this.

The production of lubricating oils differs, however, from the manufacture of glycerine in the following respects:—

1. In the lubricating oil industry extraordinarily large quantities have to be dealt with.

2. The height of the vacuum or the degree of absolute pressure plays a decisive role in the manufacture of lubricating oil, and

3. the conditions are, owing to the demands on the fractionation, considerably different.

As far as he is aware, stills larger than about 5 tons capacity scarcely come into question for the distillation of glycerine.

The first tests in the petroleum industry were, as far as his knowledge goes, also carried out with stills of this small capacity, and such stills are said to have been seen for a time in Russian

refineries. The yield from these stills was naturally small, and the particulars as to the height of the absolute pressure are unreliable. With regard to the height of the absolute pressure, it will be necessary to extend somewhat.

In the development of high vacuum distillation for the petroleum industry we can distinguish three periods so far as equipment for modern large-scale operations are concerned, which involve the treatment of quantities quite different to those dealt with in the glycerine industry—quantities of 1000 tons raw material, and more, for which, of course, the plant used in the glycerine industry would be totally inadequate.

It is, indeed, absolutely impossible to contend with such quantities in stills of 5 tons capacity.

The three periods in question are characterised by the varying degree of vacuum employed, as follows:—

(a) Distillation with low vacuum, of about 2 m. water column, therefore of about 15 cm. mercury column. Such installations were for a long time used in Europe and in America, and some are still working at the present time. The only purpose of this low vacuum was the rapid removal of the volatile products resulting from decomposition, in order to avoid their absorption by the condensed distillates.

(b) Distillation with a vacuum of about 5-6 m. water column; i.e., of about 35-50 cm. mercury column. Such installations are reported to have been used in Russia, and are still used to a certain extent in America to-day. With this moderate vacuum the reduction of the boiling point of the distillates played a small part, as may be seen from the diagram, and it was impossible to attain with it the favourable results which were achieved in the last period.

(c) By the utilisation of the high vacuum of 68-74 cm. and upwards, therefore 80-15 mm. (mercury column) absolute pressure.

It was not until this stage was reached that a rich field of gratifying work was opened up to the modern petroleum engineer.

The advantages which can be obtained by distillation with the highest vacuum possible were, as already mentioned, long known only from laboratory experiments and from tests with small distilling plant, and presumably no one will attempt to claim to have added new principles to those which have been known so long. The practical, correct application of these principles to the large operations of the petroleum industry was, however, not known, nor was its actual effect on economy in working.

As in most technical spheres, nothing can be done with the best theoretical knowledge until the engineer has found the form utilisable by the operator, and in this respect the author believes

he may claim to have created something new. High vacuum distillation was, and this is certain, not made available for the modern petroleum industry until the appropriate apparatus was devised for dealing with large quantities and until it was also practically demonstrated by the first installations that the great difficulties arising out of the constructional solution of the direct-fired, high-temperature stills and of the condensing equipment were removed.

According to information there was, prior to his devoting himself to this branch, only one high-vacuum plant of notable capacity in operation; this was in Rumania, and even after this length of time no details of it have been made known.

For large undertakings high-vacuum distillation had hitherto been *terra incognita*.

In reply to the remarks of Mr. A. A. Ashworth :—

The fuel consumption of a modern high vacuum plant depends naturally upon various conditions. It differs when very asphaltic residuum is being distilled, when asphalt-free raw material is being distilled, when sharp fractionation is required, or when, as is, for instance, the case in the distillation of paraffinoid oils, sharp fractionation can be foregone, and it is further dependent upon the quantity of distillates to be won. If 50 per cent. of the raw material is distilled off, the fuel consumption amounts on the average to 5 per cent. of the throughput.

The following results of tests carried out in the State Mineral Oil Refineries, Drohobycz, Poland, will doubtless be of interest :—

For the distillation of deparaffined paraffin-oil, with sharp fractionation, about 99 per cent. of the throughput being won as distillate, only 5½ per cent. fuel oil was necessary.

The steam consumption can, on the average, be taken as follows: For the distillation of the medium machinery oils 0·2—0·3 kg., and for the distillation of the heaviest fractions about 0·7 kg. per 1 kg. distillate is required.

With regard to the figures quoted by Mr. Ashworth, there must be an error. Every oil man would regard it as perfectly appalling if a distilling plant required 30 per cent. fuel oil for the production of 7 per cent. or even 70 per cent. distillates.

The reconstruction of a plant so wasteful would provide an agreeable task for the refiner and for the engineer.

It may be observed here that distilling plant *without vacuum*, with which about 50 per cent. of the throughput is won as distillates, requires as maximum 15 per cent. fuel oil and 0·8 kg. steam per 1 kg. distillate, and that such plant, which accordingly works under far more favourable conditions than that seen by Mr. Ashworth, can scarcely be profitable.

In reply to Mr. E. C. Craven, the author merely pointed out the theoretical statements in Dr. Gurwitsch's work, and it was, of course, not his intention to convey that Dr. Gurwitsch is the discoverer of old fundamental principles. His literary work was cited in order to avoid the inclusion of long theoretical explanations in the paper. According to the diagram shown it is, in the author's opinion, not possible to evaporate, without the application of steam, a heavy machinery oil under a pressure of 1½ m. liquid column at a temperature of 320°, even if the absolute pressure in the vapour space were nil. If steam is used when distilling, the reduction of the boiling point to 320° is, of course, feasible.

Distillation with the aid of injected inert gases, as suggested by Mr. Craven, has been repeatedly tried and has always yielded negative results. This is amply confirmed in petroleum literature (see Gurwitsch, page 208).

The remarks of Dr. Dvorkovitz are quite in agreement with the opening statements of the paper. It is probable that in the distillation mentioned by him vacuum plant such as described in category B was used. The author would, however, like to remove a misapprehension on the part of Dr. Dvorkovitz, who assumes that with higher vacuum the difficulties of continuous working increase; exactly the opposite is the case, as the lower the absolute pressure the lower the differences in pressure which can ensue between the individual stills.

Some twenty continuous distilling batteries, having a daily capacity of up to 600 tons per battery, have been working for years with entire satisfaction.

It goes without saying that such distilling plant must be provided with appropriate condensing equipment which enables differences in temperature to be avoided. The further remarks of Dr. Dvorkovitz also run parallel with the statements contained in the paper.

With regard to the remarks of Mr. W. H. Coleman, he feels certain that the old tar distilling plant to which he (Mr. Coleman) alludes comprises stills of comparatively small capacity, and it is pointed out that the stills used in modern high-vacuum plant have a capacity of about 40 tons.

The remarks of Mr. McConnell Sanders are especially noteworthy, and the author shares his view that we must have further experience before we can form a definite judgment regarding distilling plant working under the extreme vacua of 5-15 mm. mercury column and which have only recently been introduced into the petroleum industry on the other side of the Atlantic.

Mr. C. Allibone's experiences in the production of transformer oil are, indeed, extremely interesting and merit serious consideration; they will certainly give rise to further practical investigations.

Naturally, all that can be expected of the best distillation is that it shall yield the products contained in the raw material unchanged as far as possible, *i.e.*, undecomposed. In other words: If there are no heavy products present in the raw material, they cannot, of course, be created by distillation; therefore, if a raw material contains no cylinder oil, no distillation process can produce cylinder oil from it.

At this point a particularly striking case in the author's own practical experience is mentioned :—

In a refinery which had for decades, owing to its inappropriate distilling plant, scarcely been able to produce 5 per cent. of lubricating oils, approximately 45 per cent. of lubricating oils were produced after the introduction of high-vacuum plant, and it was not until this was adopted that the undertaking became profitable. In brief, the good products present in the raw material could only be won unchanged by distillation under high vacuum Needless to say, high-vacuum distillation did not create these products.

Dr. Steinschneider regrets that it was not possible for him to reply in person to the points raised in the discussion, especially as otherwise there would have been an opportunity of putting additional questions, and consequently of further elucidation of the paper.

Dr. Dunstan, to whom the author is further indebted for the trouble taken on his behalf during the discussion, has rightly observed that in continuous distillation it is a much easier matter to maintain constantly the correct relationship between steam application and distillate; and that is one of the reasons why, as already mentioned, high vacuum plant of large capacity is made in continuous working batteries. The steam consumption in such plant is unquestionably far more favourable than in discontinuous plant.

The quantity of steam, however, even in this case, exceeds the theoretical, owing to the unavoidable inadequacy of the mechanical equipment employed for the distribution of the steam.

Under all circumstances, high-vacuum installations should be so arranged that they are capable of working even under the lowest absolute pressure without imposing excessive demands upon the operators of the plant.

It is, further, essential that they be provided with dephlegmating arrangements which allow of sharp fractionation, in order to avoid expensive redistillation.

In these two requirements an early and promising field of activity for the engineer is seen, and progress in this respect is predicted in the near future.

The following contribution was received from **Mr. C. O. F. Jenkin** :—

Dr. Steinschneider states that a pressure of 45 mm. of mercury can be reached with water at 25° C. and that 20 mm. is possible under very favourable conditions.

These figures may be possible, but the pressures are very much lower than is normally the case in practice. None of the five or six benches of Bruenn-Koenigsfelder stills with which I am acquainted normally operate at anything like this vacuum. The usual pressure varies between say 75 mm. and 110 mm., and if for some special reason they manage to reach 50 mm. it is considered something of an achievement. So little are pressures in the neighbourhood of 20 mm. considered as really possible on B.K. stills that a patent has been actually granted in America and applied for in European countries of which the root idea is that the stills should work under a pressure of less than 25 mm.

As erected at present the B.K. H.V. plant works continuously and normally consists of some form of preheater, four, six, or eight stills in series under stepped vacuum, i.e., the pressure in the coolest still is in the neighbourhood of 350 mm., decreasing by steps to say 60 to 110 mm. in the hottest. When running an asphaltic oil the installation is in addition usually equipped with two montejus, also under vacuum. The residual asphalt from the last still runs into one of these, and when full, into the second. The vacuum is broken on the first and the material blown or pumped away.

The following paper was then read by Mr. E. C. Craven :—

The Determination of Unsaturateds in Petroleum Spirit.

By W. R. Ormandy, D.Sc., F.I.C.,F.C.S., and E. C. Craven, B.Sc., F.C.S. (Members).

As has been pointed out in a previous note (J.Inst.P.T. 10, 41, 1924), the term unsaturateds in connexion with petroleum spirit has a restricted meaning. The term is confined to those hydrocarbons containing one or more double bonds which absorb bromine readily under the conditions of the usual tests such as those of Hanus or Wij. It is some of these constituents which give rise, in cracked spirit in particular, to sticky resins. It may very well be, as Dr. Dunstan points out, that gum formation is due to bodies of the diene class and not to mono-olefines. Certainly such of the liquid mono-olefines, as have been prepared in a state approaching purity, appear to be very clean distilling bodies, quite suitable

for use as motor fuels. Moreover, by suitable processes of purification spirits have been obtained which, while having high bromine absorptions, yet do not deposit gum on standing or give resinous residues in the copper dish test.

No satisfactory method appears to have been devised for the determination of the proportion of unsaturated hydrocarbons present in a given sample of petrol. The present note does not claim to offer any solution of the problem, except as indicating that if several methods lead to substantially the same figure, then some reliance may be placed on the result.

The main ideas in this work were as follows. Firstly, assuming the unsaturateds present to be mono-olefines, each molecule should absorb 2 molecules of bromine. If therefore the molecular weight and the bromine absorption of the unsaturateds were known, an estimation could be made of the proportion of unsaturateds present. Secondly, if from the total loss in strong sulphuric acid the aromatic content were substracted, the difference should be the unsaturateds.

In regard to the first idea obviously many difficulties exist. All bromine absorption tests are of a somewhat empirical nature and only give more or less relative results. It is known that substitution, as well as addition, of halogen, takes place in such tests, and hence the simple relation assumed is rather doubtful. However, as some method had to be selected if progress were to be made, the Hanus test was used. This was perhaps a rather unfortunate selection, since the use of the acid Hanus reagent precludes the titration of the substitution formed halogen acids. For the determination of mean molecular weight it was assumed that this could be taken as of the same order as that of the whole spirit. It has been found in regard to one particular spirit that on fractionating, the bromine absorptions show that the unsaturateds appear to be fairly evenly spread over the various fractions.

The following figures were obtained:—

Fraction	1	to 55° C.	Bromine No.		9·2
„	2	55–95° C.	„	„	6·8
„	3	95–112° C.	„	„	5·8
„	4	Residue	„	„	4·0

The molecular weight of original spirits was determined by the Victor Meyer method in a coal gas atmosphere at 25° C. Since a small resinous residue was left in the small tubes, in most cases the tubes were re-weighed and the molecular weight of the volatile portion only is stated, together with the percentage of residue, if any. This resinous residue is no doubt of very high molecular weight and to get the true molecular weight the figure given should be increased by the proportion of residue.

In regard to the second idea the acid losses presents no particular difficulty. Where possible 100 c.c. of spirit were weighed into a funnel, shaken for half-an-hour with 300 c.c. of acid, and allowed to stand all night. The residual spirit was tapped off carefully and weighed. Aromatics were determined by the modification of the Tizard-Marshall method, in which the difference of the aniline point of the spirit after washing with 3 volumes of 80 per cent. H_2SO_4 and 3 volumes of 98 per cent. H_2SO_4 is taken as the change of aniline point due to removal of aromatics.

Opportunity was taken to determine the change in physical constants of the spirits by the action of the two acids in order more particularly to determine what is the action of the 80 per cent. H_2SO_4.

Four spirits were used:—

A = A mixture of commercial No. 3 spirits.

B = A shale petrol.

C and D = Two typical cracked spirits.

The results of the tests made on these four spirits are tabulated below:—

Test.	A.	B.	C.	D.
Sp. gr. 15·5/15·5° C. orig. ..	0·7431	0·7326	0·7703	0·7604
" after 80% H_2SO_4 ..	0·7456	0·7546	0·7724	0·7695
" " 98% " ..	0·7324	0·7370	0·7377	0·7571
nD 15·5° C.—				
Original	1·4173	1·4148	1·4302	1·4241
After 80% H_2SO_4	1·4185	1·4218	1·4326	1·4293
" 98% "	1·4079	1·4142	1·4090	1·4207
Acid loss—				
By 80% acid	2·1%	9·5%	4·5%	7·5%
By 98% acid	17·4%	34·8%	33·5%	24·3%
Aromatics	13·9%	24·8%	28·1%	14·7%
Rise of aniline point by 80% H_2SO_4 wash..	0·9° C.	6·1° C.	1·2° C.	6·6° C.
Gum test after 80% H_2SO_4 wash	small		0·6%	0·6%
Bromine absorption, original..	6·0%	59·3%	21·6%	14·0%
Molecular weight—				
Original	101	102	101	108
Residue in tube	small	small	small	small
After 80% H_2SO_4	102	109	105	116
Residue in tube	small	1·5%	0·5%	small
After 98% H_2SO_4	105	133	105	123
Residue in tube	small	small	small	small

From these figures the following may be calculated:—

	A. %	B. %	C. %	D. %
Method 1 (*a*).				
Loss in 98% acid	17·4	34·8	33·5	24·3
Aromatics	13·9	24·8	28·1	14·7
Difference	3·5	10·0	5·4	9·6
Method 1 (*b*).				
Loss in 80% acid	2·1	9·5	4·5	7·5
Gum test	—	3·0	0·6	0·6
Total	2·1	12·5	5·1	8·1
Method 2.				
Unsaturateds calc from Br. test	3·8	37·8	13·6	9·4

It would appear that the figures given by the bromine absorption is liable to be too high. With the shale petrol B, the calculated unsaturateds are higher than the total loss in strong sulphuric acid. Possibly better results would be obtained if the additive bromine only were taken, though even then the presence of bodies with multiple double bonds should tend to give high results.

The effect of the washing with 80 per cent. H_2SO_4 appears to be partly a dissolving action and partly a polymerising action. The residual spirit is slightly higher in S.G., refractive index and molecular weight. If the polymerisation were entirely to non-volatile resins, one might expect to get a reasonably good value for the unsaturateds content by adding together the loss in 80 per cent. H_2SO_4 and the residue on evaporation. Comparing the figures actually so obtained, however, with those obtained by Method 1 (*a*) they appear to be somewhat lower. This may be due to the formation of polymerised olefines volatile on the water bath. This may be the case in the A, No. 3 spirit, where the resin formation by the action of 80 per cent. acid is small. So far as can be judged the method based on the loss in the strong acid appears to give reasonable results, and these do not differ greatly from the Method 1 (*b*) figures. A further method which suggests itself is washing with 80 per cent. H_2SO_4, followed by a distillation to the end point of the original spirit. This would give a greater proportion of the polymerised olefines than the evaporation test.

At any rate, the figures given should provide some basis for discussion, and in the meantime the two methods 1 (*a*) and 1 (*b*) give results which appear to check within reasonable limits.

DISCUSSION.

The President conveyed to the authors the thanks of the Institution for their paper.

Dr. A. E. Dunstan said he supposed there was no question in the last ten years which had interested organic chemists concerned with petroleum more than that of the differentiation between the various types of hydrocarbons. The technical journals discussed innumerable attempts to solve that difficult problem. It seemed, really, that the only way to attack the question was by making up mixtures of known proportions of known bodies, and then work a method out from that. It was in some such way that the determination of aromatic hydrocarbons in motor spirit was worked out. Suppose, for example, one took a spirit boiling between 30° C. and 200° C. and washed out the unsaturateds or removed them or partly polymerised them by means of 80 per cent. sulphuric acid, a strength which had been generally accepted for this purpose. One obtained polymers which were partly soluble in the spirit and partly in the acid, and the loss of volume did not give one the figure one required. In his own laboratory he had tried the following method: If, after and before the acid treatment, one carefully fractionated between the limits of 30° and 150°, the volumetric difference would give the amount of unsaturateds actually removed. Further work on these lines was being actively prosecuted.

Dr. Paul Dvorkovitz asked whether the authors had applied the Bromine test to the original motor spirit.

Dr. R. Lessing thought Dr. Dunstan's suggestion that in order to make the position clear one ought to start synthetically and prepare known mixtures was an excellent one. The only difficulty to his mind was to get the substances required. One suggestion which might be helpful was that instead of taking a spirit of a comparatively wide boiling range it might be possible to come to closer fractions. If that were not possible—and certainly it was difficult to do with small samples in the laboratory—it might be possible to get a very narrow fraction, even less than 10°, say fractions of one degree. Such fractions could be got nowadays with ring-packed stillheads. If one would get those from different types of commercial spirits they would give definite empirical figures, and by comparison of the fractions and mixtures from them it might be possible to get a little nearer to the truth. The difficulty really was that one did not know the individual compounds that

were present, and as long as one could not make artificial mixtures, one had to adhere to empirical results which were bound to vary considerably according to the method used and the different degrees of cracking the spirit had gone through, and so on. It, therefore, seemed to him that the first thing was to narrow down the properties by getting a very much closer fractionation than was being obtained at present. Dr. Dunstan's proposal to cut out the polymerised or polymerisable fraction was a step in the same direction.

Dr. W. R. Ormandy said that the proposal made by Dr. Dunstan was very interesting, but he would like to know on what ground Dr. Dunstan assumed that polymerised bodies stayed behind in the portion that was left. Did Dr. Dunstan imply that of necessity they had a higher boiling-point than 150°, and if so on what basis did he found that view? What was being dealt with were polymerised bodies which were soluble in the petrol.

Dr. Dunstan said he could give one instance. Brooks's paper in the American Chemical Journal four or five years ago dealt with the subject in connection with the effect of acid in polymerising amylene to diamylene, and it was a matter of common knowledge that diamylene could be separated by careful fractionation from hydrocarbons of lower boiling-point.

Dr. Ormandy said that unfortunately the pure chemicals which could be obtained were not the pure chemicals which appeared in the petrols which had to be used.

Dr. Dunstan said many of them were.

Dr. Ormandy said there were very few. He had spent eight or nine months at the work, but had not yet finished finding out what bodies were present in a special petrol. If one took 200 c.c. and had to work with them, it was almost hopeless. He thought the method which had been put forward by Dr. Lessing would be very interesting, but it involved a tremendous amount of work on very small fractions, and it could only be done with the help of the oil companies; it could not be done in the laboratory.

He wished to point out that the paper started off with a large number of assumptions in any case. The oil was shaken up with 80 per cent. sulphuric acid, and something was removed and something was left. That was the first assumption. Then it was shaken up with 98 per cent. acid, and the aromatics removed. That was an assumption, and a big one. If the acid happened to be 98·5 or 99 per cent. something else would go; if it happened to be 100 per cent. a lot more would go. The amounts of naphthenes

were determined by the aniline method. In textbooks no reference was made to the difficulty of getting the aniline pure, or as to what happened if there was 0·1 or 0·2 per cent. of water present. Such an addition was very difficult to get rid of, and it had a very much bigger effect than 5 per cent. of naphthene. The best thing to do was to admit that very little was known about the subject, and until some pure chemicals could be obtained not much progress could be made. The only pure chemicals available in any quantity were pentane (and one variety of pentane differed from another more than pentane differed from the average hextane) and heptane, pure benzol and toluol, and hexahydrol benzol and hexahydrol toluol. That was about the limit, and when one had done all one's experiments with those, one would find that in most petroleums with which one had to work those were not the bodies present.

The President thought Dr. Ormandy's explanation would help readers of the Journal to understand the last paragraph in the paper—that the two methods 1 (a) and 1 (b) gave results which appeared to check within reasonable limits.

Mr. E. C. Craven, in reply, said Dr. Lessing's suggestions would be very fine if it were possible to procure known pure bodies. With regard to Dr. Dunstan's suggested method, he thought it was more or less along the lines of what was suggested in the paper. The action of sulphuric acid was partly to dissolve the unsaturateds and partly to polymerise them. One could possibly get the true value of the amount of the polymerised hydrocarbons by distillation. The principle, he thought, was exactly the same. The assumption that only unsaturated bodies were affected by 80 per cent. sulphuric acid was proving on further investigation not to be true, as was also the assumption that aromatics were removed completely, and nothing else, by 98 per cent. sulphuric acid. The whole matter was in a state of flux.

In reply to Dr. Paul Dvorkovitz :—

The bromine absorptions of the spirit A—D are given in the table. The bromine absorption of the spirit which was fractionated was 5 per cent.

The following paper was then read by Mr. E. C. Craven :—

Determination of the Molecular Weight of Petrol.

By W. R. Ormandy, D.Sc., F.I.C., F.C.S., and E. C. Craven. (Members).

In the course of some work involving the determination of the molecular weight of petroleum fractions by the Victor Meyer method it was noticed that erratic results were obtained when the temperature of the bulb was high. Since for petroleum spirits

having an end point of about 200° C. it is necessary to use a temperature of say 250° C. to ensure complete vaporisation in a reasonable time some determinations were made of the influence of the temperature on the results obtained with various bodies.

In some cases the Victor Meyer tube was heated in an electric furnace, but experiments were also made heating by the vapour of boiling liquids in the usual manner.

The following results were obtained for molecular weights. Complete vaporisation was assumed to have taken place when the displaced air appeared to remain constant over half a minute or so. The figures given are in most cases the mean of two or more determinations.

Temp. °C.	Heptane.	Shell.	Pratt's.	Benzene.
In Electric Furnace.				
200	102	100	97	77
220	73	96	96	76
250	79	98	95	78
265	74	80	78	75
275	70			
*275 plus porous pot	78			
In Vapour Bath.				
183 (aniline)	100	96	103	78
218 (naphthalene)	97	98	99	78
238 (quinoline)	73	99	99	78
285 (B-naphthol)	75	85	86	78

* A few tiny fragments of porous earthenware were put into the tube in which the heptane was weighed.

It would appear from the above figures that heptane is the most easily affected of the above bodies, low results being obtained at temperatures above 220° C. The two petrols appear to be more stable, withstanding some 250° C., whilst with benzene, as might be expected, there is no evidence of any effect up the highest temperatures employed.

It was thought at first that these effects were due solely to the cracking of the liquids since it was observed that the displacement of air took place in distinct jerks and a slight brown film, presumably "carbon," was left on the small tubes in which the liquids were weighed (benzene is, of course, excepted from all these remarks). Further work has shown that, whilst cracking does undoubtedly take place, either this is accentuated by the presence of air or actual combustion of a portion of the hydrocarbons occurs. Be this as it may, it would appear that the bulk of the action occurs whilst the bodies are in the liquid state. This is shown to some extent by the experiment with heptane in which a little piece of porous pot was put into the weighing tube. It was hoped that if the heptane would boil off readily normal results would be obtained. Whilst

this was not the case, there was obviously some improvement. The cracking action, moreover, does not seem to increase with rise of temperature above the critical, but the molecular weights obtained are more or less of the same order. This would indicate that the bulk of the cracking action is over in a comparatively short time, and hence while the body under test is in the liquid state.

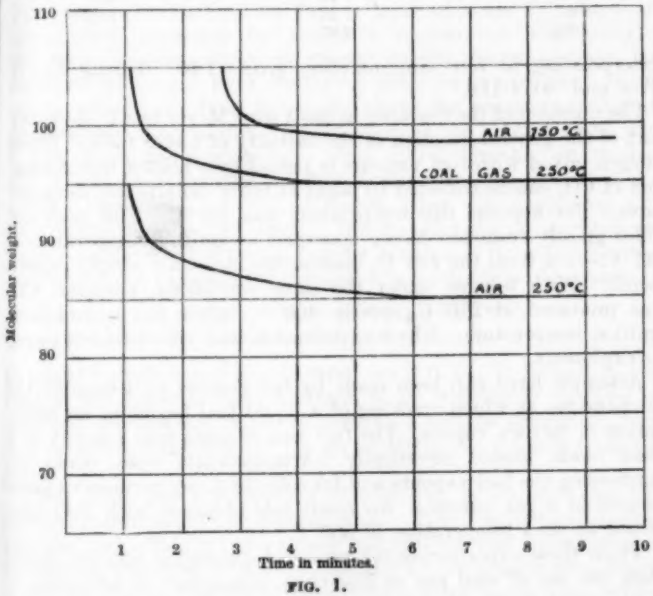


FIG. 1.

The following tests on heptane indicate this and also the effect of replacing the air in the Victor Meyer apparatus with other gases.

Temp. °C.		Gas.		Mol. wt.
250	..	Coal gas	..	95
317	..	Air	..	85
317	..	Coal gas	..	103
320	..	Carbon dioxide	..	103
375	..	Air	..	79
375	..	Coal gas	..	101

Some experiments were made in which the rate of air displacement was noted. The graph (Fig. 1.) shows the calculated molecular weights corresponding to the volume of air displaced at various times from the start of the determination.

A comparison was made with Red Line petrol of the results obtained by the Victor Meyer and Raoult methods. By the former method using aniline and naphthalene the results were 101 and 100 respectively. For the freezing-point method, phenol was used.

% petrol added. $=c.$		Lowering of f. pt. $=dO.$		$c/dO.$
1·99	..	1·17	..	1·70
2·52	..	1·47	..	1·72
4·17	..	2·28	..	1·83
4·93	..	2·67	..	1·85

Exterpolating to zero concentration gives=1·60. Taking K=74 gives mol. wt.=118.

The question of the cracking in the Victor Meyer test is obviously part of the general question of the stability of motor fuels. When oxygen mixed with fuel vapours is passed over heated iron, formation of CO_2 can be detected to begin at fairly definite low temperatures. For heptane this temperature was 241° C. This does not differ greatly from the Moore spontaneous ignition temperature—247° C.—nor from the 220° C. limit in the molecular weight experiments. With toluene under the same conditions, however, CO_2 was produced at 210° C., nearly 400° C. below the spontaneous ignition temperature. These experiments were discontinued owing to explosions.

Attempts have also been made by the authors to determine the temperature at which cracking of a liquid fuel begins in an atmosphere of its own vapour. The fuel was dropped into a cavity in a steel block heated electrically. Arrangements were made for condensing the fuel vapours and for collecting any permanent gases formed in a gas burette. No result was obtained with Red Line petrol up to a temperature of 500° C.

From these experiments the practical conclusion may be drawn that the use of coal gas or hydrogen atmosphere is advisable in determinations of molecular weights of petrols by the Victor Meyer method, and also some light is thrown upon the reactions which occur when the air atmosphere is not so replaced by hydrogen. The brown deposit on the weighing tubes may indicate that polymerisation and asphalt formation take place, and, in addition, it appears to be clear that cracking or partial combustion takes place particularly whilst the spirit remains liquid, the vapours apparently being much more stable.

The authors wish to acknowledge the financial assistance received from the Distillers Co., Ltd., and the Fuel Research Board of the Department of Scientific and Industrial Research towards the expenses of this research, and to that on the "Determination of Unsaturateds in Petroleum Spirit."

DISCUSSION.

On the motion of the President a hearty vote of thanks was accorded to the authors for their paper.

Professor J. S. S. Brame said the paper raised a very important matter. It was found that very big differences were obtained when comparatively high temperatures above the vaporising point were used. In his student days a limit of some 30° above the temperature necessary for complete vaporisation was given as the desirable temperature in vapour density determinations, and reference to an old book confirmed that the temperature should not be raised more than 30° or 40° above the necessary maximum for complete vaporisation. In the cases of the heptane dealt with in the paper, the temperatures went up considerably above that, and it was somewhere about 200° before anything abnormal was noted. One could not tell, of course, what was happening with very mixed liquids like petrol. His remarks would, therefore, be largely confined to the pure substance heptane. He would mention the well-known equation for the complete combustion of heptane :—

$$\underset{12 \text{ molecules}}{C_7H_{16}+11O_2} = \underset{15 \text{ molecules}}{7CO_2+8H_2O}$$

It might be taken as a simple ratio, say 4 to 5. It seemed to him that if the material were assumed to be completely oxidised at constant temperature with the increased volume suggested, even that would not account for the great differences referred to in the paper.

Then there was the question of coal gas, or an inert gas like carbon dioxide, being used instead of air. That was very interesting, because undoubtedly the authors had proved that these affected the action, whatever it was. Personally he could make no attempt to say what the action was, but he did not think it could be claimed that the coal gas or the carbon dioxide inhibited cracking to any great extent, though they might have some effect.

He thought the paper was a valuable one, because it indicated something which was largely unsuspected, and it was a matter that ought to be thrashed out fully so as to get to the bottom of it. He did not think oxidation was going to account for more than a very small difference between the figures, or that cracking was going to account for a great deal.

Mr. J. McConnell Sanders asked what useful purpose they would assign to the determination of the molecular weight of a non-homogeneous substance such as petrol. He admitted that investigation of heptane or any other pure hydrocarbon might

have a scientific value, but he could not see how the molecular weight *per se* of any commercial substance which was admittedly a mixture, and which was subject to a certain extent to the methods of refining employed, could ever be applied in practice, except as an indication of some other quality. If the consumer were to go to the refiner and ask him to make a petrol of a certain molecular weight, the refiner would probably reply that he could not do it, but would also probably go on to ask what would be the use of it if he could.

Mr. Gordon Pitt said that while he had no doubt that Dr. Ormandy would reply to the last speaker much more effectively than he himself could possibly do, he would like to say that there were cases on record where a very accurate scientific knowledge of matters as complicated as that of the molecular weight of petrol had practical bearings which might not previously be expected. One might almost think it was a waste of time to indulge in as complicated and laborious and lengthy a research as was necessary to determine the molecular weight of a given petrol, even if that were possible, and he was quite sure Dr. Ormandy would agree with him that it was doubtful whether it was possible. There were cases, however, where an approximate knowledge of the molecular weight of petrol had a very important bearing from a practical point of view, and to one such case he would like very briefly to refer. During the war he happened to be engaged for a considerable length of time in the Royal Air Force experimental department in investigations as to the possibilities of using various substances on aircraft at very high altitudes and therefore at very low temperatures, and one of the things that were found to be of most value in determining what petrols could be expected to behave in a normal manner with certain conditions of compression in aircraft engines, and what gave the best preliminary information which could be obtained to enable suitable petrols to be selected for tests, was the approximate molecular weights of those petrols.

Mr. A. A. Ashworth said the paper read rather like an indictment of the Victor Meyer method of obtaining molecular weight, but he thought, as a matter of fact, the tendency nowadays was to use a cryoscopic method with pure benzol as a solvent. Recently some very good work was done in the University of New York in that way on the molecular weight of gasolenes, and the method was checked showing that the molecular weight was correct to the value of one-half of one molecular unit, which was very close agreement. There were difficulties in the way of the application of that method, of course. In New York a Beckmann thermometer was used, and evidently those responsible for the experiments

were more lucky with their Beckmann thermometer than he himself had been; he could not get one to give the same readings two days running. He supposed it was possible to get a thermometer that would not vary from day to day by using a thermocouple, and by that method and by using benzol, which, as Dr. Ormandy had said, one could obtain pure, one ought to be able to get reliable results that would compare day after day and possibly provide some easier method of obtaining molecular weights, not only of petrols, but of other distillates. One might therefore obtain a good deal of insight into the variation of different oils.

Mr. D. Finlayson thought the authors' work was of the utmost importance. In connection with the carburation of motor-car engines, one of the most important practical points was to know what were the limiting temperatures and pressure necessary to allow complete vaporisation of the fuel in the fuel/air mixture. One of the methods by which that knowledge could be obtained depended on a figure for the apparent molecular weight of the petrol.

With regard to the actual cracking, or whatever was going on, he thought that was an extremely important point, and he hoped the authors would be able to clear it up and show what really was occurring. He would like to ask them how the results were affected by the air, or rather the oxygen and nitrogen, in solution in the petrol.

Dr. W. R. Ormandy said it had been stated by one speaker that the paper did not appear to act as an advertisement for the Victor Meyer method of determining molecular weights. The authors started out with the idea that it was probably, taking them all round, the most accurate and the simplest method where one had to get a figure that was accurate within one or two units. He did not want the molecular weight of petrol at minus 4° C.; what he wanted to know was what was the molecular weight about the temperature at which it went into a motor-car cylinder. The freezing-point methods, therefore, were not particularly interesting except as confirmation. They were very accurate.

An interesting point was touched on by Professor Brame, who asked why, when one heated a pentane or heptane—and it applied to any of the paraffin bodies—to a temperature as low as 250° C., there was an increased volume. The question was whether it was due to carbon dioxide plus water, which obviously did not seem to account for it, or whether it was due to a differential oxidation such as took place with ether before combustion. He did not know what the true explanation was, but it was obviously a matter of the very greatest importance in the relationship between

the petrol industry and the motor-car people who used the bulk of their output. In a motor-car engine the fuel entered the cylinder almost invariably as a mixture of vapour and liquid. The vapour itself was comparatively stable; it would stand heat to over 500° C. in the presence of iron without any appreciable cracking taking place or appreciable combustion in the case of benzol. In doing V. Meyer determinations one got brown films on the glass tubes containing the petrol. The authors anticipated working on the production of larger quantities of that brown material in order to see how it resembled the asphaltic deposits found in Diesel and petrol engines, which to a very large extent were not entirely due to the lubricating oil.

The extraordinary thing was that the decomposition temperature —the temperature at which those paraffin bodies began to decompose in the presence of air—was approximately the temperature at which they formed explosive mixtures in the spontaneous ignition apparatus with oxygen. The question was what mechanism was at work to cause the mixture of petrol or heptane vapour and heptane liquid to be able to explode with air or oxygen when the vapour itself might be heated to a much higher degree without any explosion taking place. The suggestion had been made that at the particular temperature at which that reaction took place—and it was a very specific temperature; it was not a thing which started gradually—the vapour as it was immediately formed was capable of absorbing heat and energy *quanta* from the radiation taking place at that temperature, and some experiments which corroborated that had been carried out by David and published in the Transactions of the Royal Society. As Professor Brame said, the question raised a series of problems the elucidation of which might be of the greatest value both to the oil and the motor industry. The object of the authors in putting their short paper forward was merely to draw attention to the bearing of the experiments so that others might think about them and work on them, and so fresh lines of research might be suggested.

Mr. E. C. Craven, in reply, referred to the text book quoted by Professor Brame, which said that a temperature of 30° or 40° above the necessary maximum for complete vaporisation should be regarded as the limit, and said that that would be quite a sufficient margin for bodies boiling below 100° C., but it must be remembered that when one came to deal with bodies which possessed a higher boiling-point, it was the corresponding temperatures which had to be dealt with and not differences in degrees Centigrade. For example, if for the body boiling at 50°, or say 300° C. absolute temperature, some 30° were sufficient, for a body boiling at 200° C. one would want about double the margin, because one would be

at double the absolute temperature. The authors were very much obliged to Professor Brame for his other suggestion about the small increase that was to be expected by combustion. It looked as if the formation of bodies of lower molecular weight was taking place. Personally that point had not occurred to him.

With reference to the equation given by Professor Brame the correct interpretation is surely as follows. If no combustion occurs the vaporisation of 1 molecule of heptane gives a volume of vapour which can be taken as unit :—

$$\underset{(0+11)\text{ vols.}}{C_7H_{16}\text{ (liquid)} + 11O_2} \quad \text{become} \quad \underset{(1+11)\text{ vols.}}{C_7H_8\text{ (vapour)} + 11O_2}$$

The air displaced is therefore 1 volume.

If complete combustion occur :—

$$\underset{(0+11)\text{ vols.}}{C_7H_{16}\text{ (liquid)} + 11O_2} \quad \text{become} \quad \underset{(7+8)\text{ vols.}}{7CO_2 + 8H_2O}$$

The air displaced is therefore 4 volumes. Hence a molecular weight of only one quarter the true value would be obtained.

As for the practical use of the determination of the molecular weight of petrol, some of the speakers had discussed that to some extent, but it certainly gave a good measure of the latent heat of a petrol, which was a constant that was sometimes wanted in regard to the use of petrol in internal-combustion engines. The value of research of the kind in question had also been pointed out by Mr. Gordon Pitt. With regard to the use of cryoscopic methods for the determination of molecular weight, one might get very concordant results if one could use similar concentrations, but in a solvent one had the association of the body whose molecular weight one was determining. For example, with benzene in phenol or acetic acid one could get values ranging from 80 to 130 as the proportion of benzene increased. One had to exterpolate to zero concentration before one could get an accurate value. If hydrogen or coal gas were employed in the Meyer tube determinations of molecular weight could be carried out rapidly and easily to a quite sufficient degree of approximation.

The Hydrogenation and Desulphurisation of Norfolk Shale Oil.

By H. G. Shatwell, B.Sc. M.Sc. (Tech.).

Many attempts have been made to utilise the deposits of oil shale which occur on a large scale in Norfolk, Dorset and several East-Midland counties. The existence in these regions of shale, rich in oil-forming constituents, has been known for many years, but the numerous types of retort experimented with have failed hitherto to give an oily product which is amenable to any known method of refining.

The Kimmeridge shales, outcropping in Norfolk, are particularly abundant, are easily mined and yield on distillation substantial quantities of oil, ammonium sulphate and combustible gas. Forbes-Leslie, who has carried out investigations of the deposits, states that the products per ton of shale retorted are 40 gallons of oil, 66 pounds of ammonium sulphate and 25,000 cub. ft. of gas.[1] The yields are therefore greater than in the case of Scottish shale, but the properties of the respective oils are fundamentally different.

Forbes-Leslie describes Norfolk shale oil as being golden-black in colour, with a purplish tint by reflected light and despite its high specific gravity of 0·942 to 0·960, is very mobile. It possesses a very high percentage of sulphur, sometimes of the order of 7·8 per cent. (*loc. cit.* 24), and contains 3 to 4 per cent. of bases, 3 to 4 per cent. of phenols, cresols, etc., and 3 to 4 per cent. of benzol and toluol. Fractionation of the oil in field trials resulted as follows:—

	%
0° to 185° C.	23·3
185° to 250° C.	24·6
250° to 300° C.	20·8
Above 300° C.	31·3

A sample of the crude oil has been examined by Blackler, who concluded that it was composed of 20 per cent. of sulphur-free saturated hydrocarbons, 50 per cent. to 60 per cent. of olefines and diolefines and 20 per cent. of sulphur compounds.

Recently, Challenger, Jinks and Haslam[2] have isolated thiophene and 2-methylthiophene from a specimen of the crude oil.

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[1] *Journ. Inst. Petr. Techn.*, **3**, 24, 1916.

[2] *J. C. S. T.*, 1925, **127**, 162-166.

The characteristics of Norfolk shale oil, therefore, are such that its refining presents several problems. In the first place, if products comparable with those prepared from natural petroleum or Scottish shale oil are desired, the sulphur compounds must be almost completely eliminated. Since such substances have been estimated to comprise 20 per cent. of the crude (*loc. cit.*), heavy refining losses may be anticipated. Secondly, as the sulphur is present in the form of thiophenes and other compounds of unusual stability, their elimination will be a matter of no small difficulty. Finally, attempts to deprive the finished products of sulphur will, in the majority of cases, simultaneously remove the unsaturated hydrocarbons, many of which may be valuable constituents, and lead to refining losses, which will render commercial application impracticable. Hitherto, the sulphur difficulty has attracted most attention, but all efforts to reduce its content of sulphur to a satisfactory figure have failed and winning of the shale, in consequence, has almost ceased.

It was thought, therefore, that it would be of theoretical and practical interest to submit the oil to hydrogenation under conditions of high pressure and temperature (Bergius Process), since Bergius has claimed that such treatment results in the elimination of sulphur as hydrogen sulphide.[3] "Berginisation," therefore, presents a method of attack which does not appear to have been studied previously. It is conceivable, indeed, that hydrogenation may not only bring about decomposition of the sulphur compounds present in the oil, but that it may simultaneously reduce the unsaturated hydrocarbons and render subsequent refining less difficult.

Examination of the Crude Oil.

The sample of shale oil used in the following experiments was kindly supplied by Messrs. English Oilfields, Ltd. It was a dark-brown to black mobile liquid with an offensive odour, which was intensified on heating, and it was found of advantage during distillations to pass the uncondensable gases through strong nitric acid to prevent the escape of nauseous odours. The crude oil was miscible with strong sulphuric acid in all proportions, the mere mixing of the two liquids giving rise to a violent reaction, the heat of which was frequently sufficient to cause the oil to boil. The specific gravity at 15·5° C. was 0·9850, sulphur content by bomb method 6·81 per cent. and iodine value (Wij's) 882.

[3] E.P. 4574, 1914; 5021, 1915; 192, 849, 1923.

Engler distillation of 100 c.cs. of the oil gave the following results :—

Initial Boiling Point	105° C.
Distillate to 100° C.	nil.
„ „ 125° C.	„
„ „ 150° C.	1%
„ „ 175° C.	6
„ „ 200° C.	14
„ „ 225° C.	20
„ „ 250° C.	29·5
„ „ 275° C.	39
„ „ 300° C.	48·5

The distillate was coloured from the commencement of distillation, whilst the final boiling point was too high for determination in a glass flask. The petrol fraction boiling below 175° C. and the kerosene fraction from 175° to 300° C. were respectively light-yellow and orange in colour when freshly obtained, but both distillates rapidly darkened on standing, and in a few days had acquired the intense dark colour of the orginal crude. The residue was still very mobile. The percentages of distillates given above do not correspond with those quoted by Forbes-Leslie (*loc. cit.*), but the discrepancies may be due to different methods of retorting the shale and/or the weathering and uncertain age of the sample.

The following table shows the essential properties of the three main fractions.

Distillate.	Specific Gravity at 15·5° C.	Sulphur Content %
Below 175° C.	0·8885 ..	10·08
175° to 300° C.	0·9634 ..	7·44
Above 300° C.	1·0122 ..	6·11
Crude oil	0·9850 ..	6·81

It will be observed that the sulphur compounds predominate in the lowest boiling fraction, a property which is contrary to that of most crude petroleums.

Attempts to refine the petrol and kerosene distillates by the usual acid and alkali treatments were unsuccessful, as complete solution in concentrated sulphuric acid occurred. Even with 60 per cent. acid, separation into two layers, after agitation, was extremely slow and the loss of oil was excessive.

Experimental.

The apparatus employed in the treatment of the oil consists of a gas-heated cylindrical autoclave, capable of being rotated in a horizontal position and specially manufactured to withstand high

internal pressures at temperatures up to 500° C.[4] In each experiment, 500 c.cs. of the crude Norfolk shale oil were charged into the bomb and hydrogen or nitrogen admitted from a cylinder to the initial pressure shown in the appropriate table. The temperatures and pressures were noted at intervals of 30 minutes and heating so regulated that the temperature of the interior of the vessel was maintained at about 400° C. for three hours. The residual gases at the end of an experiment were not analysed.

In order to gain a better insight into the mechanism of hydrogenation, a blank experiment was performed in which nitrogen was used instead of hydrogen. The condition were otherwise very similar and the products were dealt with in the same way.

Experiments I. and II.—Hydrogenation and "Cracking" of Norfolk Shale Oil.

The half-hourly readings of temperature and pressure are shown in Table I. and are plotted in the graph.

TABLE I.—EXPERIMENTAL DETAILS.

Time Periods.	Expt. I. Hydrogen. Temp. ° C.	Press. (atm.)	Expt. II. Nitrogen. Temp. ° C.	Press. (atm.)
0	15	32	12	43
1	60	40	88	58
2	156	56	176	72
3	245	67	245	87
4	309	76	308	100
5	368	88	352	113
6	404	99	396	129
7	410	102	404	139
8	412	104	408	142
9	407	103	398	148
10	408	102	398	149
11	390	100	397	150
12	406	103	398	152
Final when cold	15	28	15	46
Loss in Pressure		4		—
Increase Pressure		—		3
Liquid recovered	450 c.c.		430 c.c.	
Treatment loss	10%		14%	

Reference to the graph shows that in the "cracking" experiment, the pressure began to rise rapidly at about 395° C. and continued to do so even when the temperature was allowed to fall slightly, whilst the final pressure exceeded the initial by 3 atm. During hydrogenation, however, the sudden pressure increase took place at 408° C., but was neither so marked nor continuous as during "cracking," the final pressure also being less that the original by 4 atm. These phenomena have been referred to previously.[5] The loss

[4] *Journ. Inst. Petr. Techn.*, **10**, 2, 1924.
[5] *Journ. Inst. Petr. Techn.*, **10**, 4, 1924.

in pressure of 4 atm. in Expt. I. indicates that 10 litres of hydrogen had been absorbed by the oil, together with a further quantity, represented by the hydrogen "deficiency" of the residual gas, but which was not determined.

The gases evolved in each case contained substantial proportions of hydrogen sulphide, which was characterised by its odour and its effect upon lead acetate paper.

The crude products from both experiments were very mobile, smelled strongly of sulphuretted hydrogen and were less dark in colour than the original crude.

Their other properties are tabulated below:—

TABLE II.—PROPERTIES OF PRODUCTS I. AND II.

Property.	Original Crude Oil.	Product I. Hydrogenated.	Product II. Cracked.
Specific Gr. at 15·5° C. ..	0·9850	0·9463	0·9712
Sulphur Content ..	6·81%	5·01%	5·93%
Engler Distillation:			
I.B.P.	105° C.	60° C.	58° C.
Distillate to 100° C. ..	nil.	6·5%	2·6%
„ „ 125° C. ..	nil.	8·8	5·2
„ „ 150° C. ..	1%	15·0	10·4
„ „ 175° C. ..	6·0	22·3	21·2
„ „ 200° C. ..	14·0	30·0	26·0
„ „ 225° C. ..	20·0	40·5	37·2
„ „ 250° C. ..	29·5	49·0	45·2
„ „ 275° C. ..	39·0	57·0	54·4
„ „ 300° C. ..	48·5	64·0	64·0
Yields on original Oil:			
Petrol	6·0%	20·0%	18·2%
Kerosene	42·5	37·5	36·8
Residue	51·5	42·5	45·0

It is apparent from the above that the "cracked" oil is intermediate in properties between the hydrogenated product and the untreated shale oil. The densities and sulphur contents of both products have been reduced and the percentages of contained light spirit materially increased.

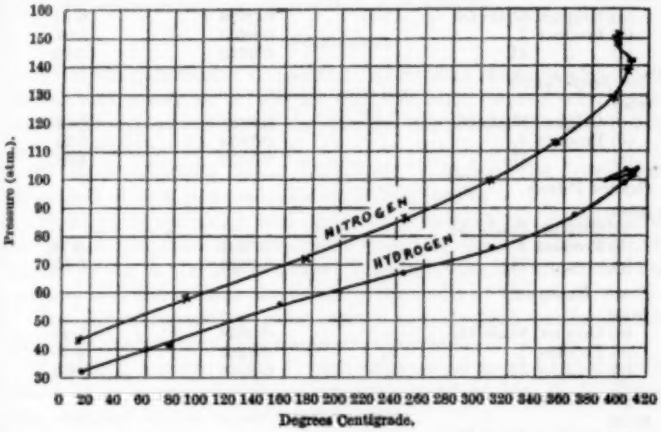
In all the above mentioned respects, the product of Expt. I. is superior to that of Expt. II., and it is evident that hydrogenation induces a greater degree of decomposition than does "cracking" under comparable conditions.

Distillation of the products was not accompanied by the evolution of offensive odours as is characteristic of the shale oil itself. The petrol and kerosene fractions in each case were only slightly coloured, but they darkened rapidly on standing.

Refining of the Products.

The treated oils were refined under identical conditions as follows. Distillation of 300 c.cs. was effected from a glass flask

fitted with a four-pear fractionating column, steam superheated to 120° C. being admitted when the temperature of the issuing vapours had increased to 150° C. The petrol and kerosene fractions were collected separately and freed from the accompanying water. They were then refined by agitation successively with (*a*) 10 per cent. of 10 per cent. caustic soda; (*b*) 2 per cent. of 98 per cent. sulphuric acid; (*c*) alkali wash repeated; (*d*) water. A mechanical shaker was used for the operations, one hour being the period of agitation in each case. The refined dry oil was then submitted



to a final distillation, the residue from the petrol fractions being added to the appropriate kerosene. Refining by the above scheme proceeded smoothly, there being no difficulty in obtaining a rapid separation in the acid wash. The losses, however, tabulated below, were high, despite the fact that only 2 per cent. of concentrated sulphuric acid had been employed.

Refining Losses.

Fraction.	Product I. (Hydrogen).	Product II. (Nitrogen).
Petrol	35·4% ..	23·0%
Kerosene	24·7% ..	26·7%

The refined products in all cases were water-white in colour, but they darkened very slowly on standing. The "cracked" oils possessed this property in the greater degree, especially the kerosene, but it was several weeks before any serious deterioration could be

detected. The hydrogenated gasoline possessed a markedly sweet odour, whereas the smell of the "cracked" gasoline and of the two kerosenes was reminiscent of that of the original shale oil.

Hydrogenation and "cracking" under high pressures had therefore effected a considerable improvement in the oil in that refining had been simplified and products of greater value obtained.

TABLE III.—PROPERTIES OF THE OILS AND DISTILLATES.

Oil.	Specific Gravity.	Sulphur Content.
		%
Crudes		
(*a*) Original Shale Oil	0·9850	6·81
(*b*) Product I.	0·9463	5·01
(*c*) „ II.	0·9712	5·93
Unrefined Petrols from		
(*a*) Original Shale Oil	0·8885	10·08
(*b*) Product I.	0·7874	5·71
(*c*) „ II.	0·8139	6·75
Refined Petrols from		
(*a*) Original Shale Oil	—	—
(*b*) Product I.	0·7646	2·78
(*c*) „ II.	0·7894	5·53
Crude Kerosenes from		
(*a*) Original Shale Oil	0·9634	7·44
(*b*) Product I.	0·9265	5·25
(*c*) „ II.	0·9266	5·98
Refined Kerosenes from		
(*a*) Original Shale Oil	—	—
(*b*) Product I.	0·9067	5·39
(*c*) „ II.	0·9073	6·10
Residues from		
(*a*) Original Shale Oil	1·0122	6·11
(*b*) Product I.	1·0207	4·48
(*c*) „ II.	1·0758	4·92

These results show that from the standpoint of desulphurisation, "Berginisation" and high-pressure "cracking" of Norfolk shale oil are only partially successful. With regard to the gasoline fractions, hydrogenation has undoubtedly produced a superior product, but at a greater refining loss. The higher fractions exhibit only slight differences in properties and it is notable that the scheme of refining adopted has given refined kerosenes which contain a higher sulphur content than the unrefined kerosene fractions. This is doubtless due to the preferential elimination of unsaturated hydrocarbons in the acid wash.

The refined petrol fraction from Product I. was subjected to further refining with 2 per cent. of acid, followed by alkali and water-washes. The refining loss experienced was 6 per cent. and the operation reduced the content of sulphur from 2·78 to 2·31 per cent. Thus it would appear that the sulphur compounds still present in the oil can only be removed by drastic treatment, necessitating uneconomic wastage.

Estimations of sulphur were conducted throughout by combustion of the substances, with oxygen, in a Mahler-Kroker bomb and specific gravities by means of a pyknometer.

Summary.

(1) Hydrogenation or "cracking" of Norfolk shale oil at temperatures and pressures of 400° C. and 100 atm. respectively, causes partial desulphurisation of the oil and increases the yield of low-boiling constituents.

(2) Hydrogenating and "cracking" under the conditions described do not give radically dissimilar results.

(3) High temperature and pressure treatment of Norfolk shale oil is not proposed as a practical means of dealing with the substance owing to the heavy losses experienced during treatment and refining and the serious corrosion of the walls of the plant.

The above researches were carried out in 1923 in the Mining Research Laboratory, Birmingham University.

My thanks are due to Mr. J. Ivon Graham for much helpful advice during the course of this investigation, and to Mr. F. H. Price, who assisted in the experimental work.

Free Sulphur in Benzole.

By W. R. Ormandy, D.Sc., F.I.C., F.C.S., and E. C. Craven, B.Sc., F.C.S.

The free sulphur content of motor fuels is a matter of great importance in relation to the corrosive effect of the fuels on brass and copper fittings. A short account was given in this Journal (1923, 577) of a method devised for the determination of this free sulphur content. The method consists in shaking the fuel with mercury, filtering off the mercury sulphide on an asbestos plug, and then dissolving the sulphide in a hydrochloric acid with potassium chlorate. The sulphate formed is determined by barium precipitation in the usual manner. On weighed quantities of sulphur the following results were obtained :—

Sulphur taken.	Sulphur found.
mg.	mg.
1·0	1·0
2·0	2·1
3·0	3·0
4·0	4·3
5·0	5·3
6·0	6·2
7·0	7·0
10·0	9·6

Other tests showed a similar degree of concordance.

The question has recently been under investigation by the research staff of the National Benzole Association. Their report is contained in the second Report of the Joint Benzole Research Committee, 1925. Owing to the alleged difficulty of the method of filtration described in the original method a modification was introduced. This modification consisted in decanting off the mercuric sulphide from the mercury, which was then washed repeatedly with the filtrate until the whole of the sulphide appeared to be transferred to the asbestos filter contained in a Gooch crucible. The crucible was then placed in a small beaker, and hydrochloric acid was poured on, followed by a few crystals of potassium chlorate. After the sulphide had dissolved the crucible was washed through with distilled water, and the determination completed in the usual manner. It is stated that up to 2 mg. of sulphur per 100c.c. satisfactory results were obtained, but that

for greater amounts low and inconsistent results were obtained. The following figures are given :—

Sulphur taken. mg.	Sulphur found. mg.
0·4	0·6
2·4	2·3
4·0	2·7
4·8	4·2
6·0	2·5
7·5	2·6
10·1	3·6

The authors ascribe these poor results to loss of hydrogen sulphide, and then further make the astounding statement that the loss of sulphur as hydrogen sulphide took place, *even when the potassium chlorate was added to the acid before treating the precipitate*. This is obviously in the highest degree improbable. The quantitative results are given as :—

Sulphur taken. mg.	Sulphur found. mg.
7·5	3·9
7·5	3·3
6·0	1·9

Since this report may be read as discrediting the original method, a few tests were made in this laboratory on solutions of sulphur in benzene, though these were really unnecessary, considering the original work. The following results were obtained :—

	Sulphur found.	
Sulphur taken. mg.	Original method. mg.	N.B.A. modification. mg.
7·0	6·6	4·2
7·0	6·8	—
10·0	9·5	5·6
10·0	9·7	6·2

It is quite obvious that the original method as described is perfectly satisfactory for the determination of free sulphur in benzole, and that the failure of the N.B.A. research staff to obtain good results is due to the modification introduced into the method. This modification is quite unnecessary, since in over a hundred tests no trouble has been experienced with the filtration of the mercury from the sulphide. It is also obvious that loss of hydrogen sulphide will not account for the low results, since there is just as much chance in the original method as in the modified method for this loss to occur. Moreover, if the chlorate acid mixture is poured on to the precipitate, it is manifestly impossible for loss of hydrogen sulphide to take place.

The reasons for the low results obtained by the N.B.A. workers appear to be two in number. Firstly, it is impossible to decant the

mercuric sulphide completely from the mercury. This can easily be observed, especially if the washed mercury be shaken with strong hydrochloric acid when the residue of sulphide collects together. Secondly, when the acid chlorate mixture merely percolates into the asbestos pad carrying the sulphide, oxidation to sulphate is only partial, sulphur being set free. It has been found that Jena sintered glass Gooch crucibles will separate the mercuric sulphide very well in the test, but owing to the acid not getting freely to the sulphide, sulphur separation occurs and the results are always low. Direct experiment on mercuric sulphide separated by decantation also shows that sulphur separation occurs when the acid supply is restricted. There is, of course, no reason to suppose that the original method cannot be improved in detail, but in result it is quite sound.

In the accompanying note Dr. A. E. Dunstan describes a modification of the method worked out in his laboratory by Mr. S. T. Card which has distinct advantages. It is, of course, quite impossible by the original method to separate every trace of mercury, not that this matters, but the use of aqua-regia is no doubt an advantage.

Some time ago occasion arose for obtaining data concerning the amount of free sulphur present in petrols. The Ormandy method was tried, and after some experiment the modifications mentioned below were made :—

1. It is agreed that it is quite impossible to separate the mercuric sulphide from all the mercury.

2. It was decided to use two thicknesses of filter-paper in the Gooch crucible instead of the asbestos pad. Using a good vacuum, most of the mercury is sucked through the wet paper, but all the sulphide is left.

3. Aqua-regia is employed as an oxidising agent in place of HCl and chlorate. With aqua-regia there is no possibility of any free sulphur escaping oxidation, and it easily dissolves the excess free mercury.

4. The crucible, paper and residue are all placed in a beaker containing the aqua-regia. It is not thought possible to wash all precipitate from the sides of the crucible, and, anyhow, neither aqua-regia nor strong hydrochloric acid are convenient liquids to wash with.

5. After boiling for some time the sulphide and mercury are dissolved, and the paper is left in the form of fine shreds. The crucible is removed from the acid by a glass rod and washed with hot water. The barium precipitate can be brought down and the paper shreds filtered off, together with the $BaSO_4$, and the precipitate ignited as a whole. The shreds, however, caused the filtration

and washing to be rather slow, therefore the shreds are now filtered off before precipitation.

The method employed is as follows:—

100 c.c. of spirit are shaken with 1-2 c.c. of clean mercury in a tap funnel for 1 hour. A little very dilute HCl is then added, and the funnel is again shaken one minute to coagulate the precipitate in the water layer. A Gooch crucible is prepared having two thicknesses of wet analytical filter-paper at the bottom. The funnel is supported above the crucible and the liquid is filtered under vacuum in the usual way. Done in this way, the mercury is first sucked through, and then the aqueous layer containing the precipitate. Thus the precipitate fills up the pores of the paper, and the spirit which follows, which is the most difficult to filter cleanly, comes through carrying only a trace of sulphide with it. If the liquid is first decanted into a beaker and the mercury is put through last, it is often very difficult to suck through. The precipitate is then sucked as dry as possible, and the crucible with the precipitate is placed in a beaker and covered with aqua-regia. The whole is boiled until no mercury globules are left. The crucible is removed by a glass rod, washed with water, and the acidic liquid neutralised with NH_4OH. One c.c. of concentrated HCl is then added, and the liquid is made up to 350 c.c. The shreds of paper are then filtered off and well washed, and $Ba(NO_3)_2$ is added to the filtrate, which is boiled and kept warm for four hours before filtering in the usual manner.

Mixtures of free sulphur in spirit were made up, using mercury-washed spirit and crystallised sulphur.

Free S present.	Found.
A. 0·014% (10 mg. per 100 c.cs.)	0·013%
B. 0·010% (7·3 mg. per 100 c.cs.)	0·009%
C. 0·015% (10·9 mg. per 100 c.cs.)	0·014%

The general results appeared quite satisfactory, though the above modifications are regarded as important to the degree of accuracy obtainable. No benzols were examined. One point appears to be important in making up the standard solutions of free sulphur. The sulphur must be recrystallised, and, to obtain reasonably quick solution in spirit, must be finely divided.

The Importance of the Edeleanu Process.[1]

By H. I. Waterman, Ph.D., and J. N. J. Perquin.

This research work was carried out at the invitation of the Allgemeine Gesellschaft für Chemische Industrie, Berlin, to assist them with different experiments, and to undertake our own research work in connection with the different applications of extraction with liquid SO_2, as used in recent years by them. The theory of the extraction process with liquid SO_2 may be supposed to be known generally, and a recent survey is to be found in the paper by Edeleanu.[2]

For the laboratory apparatus, a semi-commercial plant in which the counter current principles could be applied,[3] could be used, and in this the different materials are easily handled without discharge of gaseous SO_2 into the laboratory atmosphere.

Experiments were carried out at Berlin and continued in part at Delft University regarding the refining of Venezuela kerosene, transformer oil and the preparation of oils for medicinal purposes from a Russian crude oil distillate, while additional data were given regarding the preparation of high-test burning oil from Californian kerosene, the refining of Mexican kerosene and Californian transformer oil so that there results a commercial product of low sulphur-content giving but little "sludge," and finally the preparation of Technical "Weiszöl" from a Russian distillate and of an oil for medicinal purposes from a heavy Californian distillate. The Berlin experiments were chiefly made by Dr. A. Lazar and his colleagues (Dr. E. Hundsdörfer and others), and were partly controlled at Delft, while other parts of the research work were made by the authors at Berlin and at Delft—*e.g.*, the determination of the bromine value, the aniline point, and the experiments in connection with the exposure of the products to the rays of a quartz burner.

Experiments with Venezuela Kerosene, and the results obtained by the "A.G.F.C.I." at Berlin with Californian and Mexican kerosene distillates (Tables II. and III.). Here stress was especially laid upon the colour, odour and smoke test of the products obtained. The degree of desulphurisation was

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[1] Compare *Chem. Weekblad* **22**, 389, 1925.
[2] Edeleanu, *Z. f. angew. Chem.* **36**, 573, 1923.
[3] Edeleanu, *l. c.* **37**, 545, 1924.

also determined, and the results compared with refining with sulphuric acid and oleum respectively. It was found that the Edeleanu process, especially when followed by a final treatment with relatively small quantities of sulphuric acid and oleum, gives excellent final products, which are able to stand the most rigorous tests (Table I., Venezuela kerosene; Table II., Californian kerosene; Table III., Mexican kerosene).

TABLE I.

EXPERIMENTS WITH VENEZUELA KEROSENE.

1. Treatment in counter current with 70 per cent. by volume of SO_2 at −10° C.
2. Final treatment of the SO_2-refined oil with ½ per cent. sulphuric acid (66° Bé.) and 2 per cent. oleum (20 per cent. SO_3).
3. Silica-gel treatment of the Venezuela kerosene with 100 per cent. by weight of silica-gel, shaken for 1 hour at room temperature.
4. Treatment of the Venezuela kerosene with 2 per cent.+5 per cent. sulphuric acid.

			Edeleanu method with SO_2.		
	Original kerosene.	Treated with 2%+5% H_2SO_4 (66° Bé.).	SO_2-refined-oil (yield 80%, extract 20%)	Final treatment of SO_2-refined oil with ½% H_2SO_4 +2% oleum.	Silica-gel-refined oil.
Sp. gr. at 15° C. ..	0·818	0·814	0·803	0·800	0·816
Colour	Pale yellow.	Water-white with blue fluorescence.	Yellow-white.	Water-white.	Almost without colour.
Odour	Disagreeable.	Normal.	Normal.	Agreeable.	Normal.
Unsaturated hydrocarbons (Krämer-Böttcher) ..	16%	—	—	—	—
Bromine number, method of McIlhiney (addition)..	0·0	—	—	—	—
Critical dissolution temperature with aniline 1 : 1* ..	52° C.	53·9° C.	65·2° C.	66·4° C.	54·1° C.
Sulphur, %.. ..	0·29	0·075	0·055	0·019	0·114
Smoke-test ..	—	Positive.	—	Negative.	—

* Crude oil treated with acid by the method of Krämer-Böttcher, dissolution temperature 66·9° C. SO_2-refined oil treated with acid by the same method, dissolution temperature 68·2° C.

It is much better to first remove, by physical methods, those substances which will consume large quantities of sulphuric acid (extraction with SO_2), and then to refine the resulting product with a much smaller percentage by weight of sulphuric acid.

TABLE II.

CALIFORNIAN KEROSENE DISTILLATE.

Preparation of High-Test Burning Oil.

Properties, yield and consumption of raw materials.

			Edeleanu method with SO_2.		
	Original kerosene.	Treated with 2% H_2SO_4 + 25% oleum	SO_2-refined oil.	Final treatment of SO_2-refined oil with ½% H_2SO_4 + 2% oleum.	SO_2 extract.
Yield in % of weight calculated on distillate	—	76	77	75·5	23
Real loss calculated on distillate ..	—	24	—	1·5	—
Consumed raw materials in % of wt.: SO_2	—	—	0·3*	0·3	—
Sulphuric acid, 66° Bé.	—	2·0	—	0·38	—
Oleum (20% SO_3) .	—	25·0	—	1·5	—
NaOH solution ..	—	1	—	0·3	—
Sp. gr. at 15° C. ..	0·834	0·812	0·813	0·812	0·901
Sulphur in % of wt.	0·32	0·01	0·08	0·01	1·0
Smoke test ..	Very bad.	Good.	Not sufficient.	Good.	—
Colour	Pale-yellow.	Water-white.	Water-white.	Water-white.	Dark yellow.

* Many years' experience has proved that this generally is the percentage loss of SO_2 in the refinery.

When the original product is treated immediately with sulphuric acid, the organic material is not necessarily consumed or destroyed.

In this connection it is of importance that the results obtained in Berlin by the "A.G.F.C.I." show that the loss of SO_2 is under 1 per cent. (0·3 per cent., Tables II. and III.). In addition the construction of the large scale research plant has been carried out in such a manner that the workmen are not affected by gaseous SO_2.

The most important point of the Edeleanu method is that it enables, practically without any loss of materials, crude oil distillates to be separated into two parts which are different in chemical character and which can therefore be better treated separately on further refining.

Stress must be laid on the fact that the desulphurising action of the liquid SO_2 is very strong.

The sulphur content of the Venezuela kerosene has been lowered from 0·29 to 0·055 per cent., a decrease of 0·235 or more than 80 per cent.; with the Californian and Mexican kerosenes this

decrease is 0·24, or 75 per cent., and 0·93, or more than 80 per cent., respectively. A final treatment of the refined oil with sulphuric acid lowers the percentage of sulphur still more. When this is compared with the results obtained with silica gel, then it is seen that, with the Venezuela kerosene 100 per cent. by weight of silica gel does not give such a good result (Table I.). The desulphurisation here was 0·176, or more than 60 per cent. With

TABLE III.

MEXICAN KEROSENE DISTILLATE.

Yield and Properties.

		Without SO_2		Edeleanu method with SO_2.		
	Original kerosene.	With 2% sulphuric acid.*	With 2% sulphuric acid and then 23% oleum.	SO_2-refined oil.	Final treatment of SO_2-refined oil with 1% H_2SO_4 + 2% oleum.	SO_2-extract.
Yield in % of weight calculated on distillate	—	94	77	77	76	23
Real loss calculated on distillate	—	6	23	—	1	—
Consumed raw materials in % of weight :						
SO_2	—	—	—	0·3	0·3	—
Sulphuric acid, 66° Bé	—	2	2	—	0·38	—
Oleum (20% SO_3) ..	—	—	23	—	1·5	—
NaOH	—	0·5	0·6	—	0·3	—
Sp. gr. at 15° C. ..	0·813	0·813	0·793	0·792	0·791	0·873
Sulphur in % of weight	1·13	1·03	0·04	0·20	0·038	3·72
Colour	Yellow.	Yellowish.	Water-white.	Almost water-white.	Water-white.	Dark yellow.

* To prove that a treatment of the original oil with small quantities of sulphuric acid is quite insufficient.

Mexican kerosene also the desulphurising action of silica gel seems to be less strong,[4] although the oils used are not quite the same in both experiments. The same restriction must be made for the hypochlorite-process of *Dunstan*, with which a desulphurising of 68 per cent. was obtained when working with a Mexican distillate.[5] The bromine number (addition) of the crude Venezuela

[4] See H. I. Waterman and J. N. J. Perquin, "Desulphurising of Crude Oil Distillates by means of Silica Gel," *Chem. Weekblad* **22**, 378, 1925; *Brennstoffchemie* **6**, 255, 1925.

[5] H. I. Waterman and J. H. Heimel, *Chem. Weekblad* **21**, 374, 1924; *Journ. Inst. Petr. Techn.* **10**, No. 46, 812, 1924.

kerosene was nearly O, therefore the behaviour of the refined oil towards bromine (unsaturation) was not investigated. Important results were obtained by the anilinepoint method, using equal volumes of the oil and fresh distilled aniline.[6] Here, where an important change in the quality of the hydrocarbons has occurred, an important change of the aniline point can also be expected.

From the determinations it follows that the treatment with 2 per cent.+5 per cent. of sulphuric acid of 66° Bé., and also the refining with silica gel, does not increase the aniline point to any extent; 52° C. for the crude kerosene, 53·9° C. for the sulphuric acid-refined oil, and 54·1° C. for the silica gel-refined oil. On the contrary, the extraction with liquid SO_2 has lowered the aniline point (65·2°), while the final treatment of the refined oil with ½ per cent. of sulphuric acid (66° Bé.) and 2 per cent. of oleum (20 per cent. SO_3) practically does not increase the aniline point (66·4°). When treated with much sulphuric acid, as in the determination of unsaturated hydrocarbons (method of Krämer and Böttcher), the aniline point of the crude Venezuela kerosene was raised to 66·9°; the SO_2-refined oil when submitted to the same treatment gave an aniline point of 68·2° C.

The crude Venezuela kerosene, together with the more or less refined products, and also the SO_2 extract, were exposed, in closed tubes of Uviolglass, to the action of a quartz burner (temperature 30°F.) and the results are tabulated below:—

	Colour.	
	Before.	After 23 hours.
Crude Venezuela kerosene	Pale yellow.	Yellow.
Crude Venezuela kerosene, treated with 2%+5% H_2SO_4 (66° Bé).	Water-white.	Pale yellow.
Venezuela SO_2-refined oil	Almost colourless.	Pale yellow.
SO_2-refined oil after a final treatment with ½% H_2SO_4 and 2% oleum	Water-white.	Very pale yellow
Silica gel-refined oil	Almost colourless.	Yellow.
SO_2 extract (S content 1·13%)	Yellow-brown.	Yellow.

From this it follows that the refined oil, after a final treatment with ½ per cent. of sulphuric acid and 2 per cent. of oleum, behaves in the best way; the SO_2-refined oil and the sulphuric acid-refined oil have both become pale yellow, while the colour of the silica gel-refined oil is the most intensive (yellow). It is very remarkable that the colour of the extract becomes paler. From these experiments we may conclude, with great probability, that the

[6] Tizard and Marshall, *J. Soc. Chem. Ind.* **11**, 20 T, 1921. Also Waterman and Perquin, *Rec. Trav. chim.* **41**, 192, 1922.

observed formation of colours is caused by small quantities of determined substances. It was found that the temperature of dissolution with aniline remained unaltered for the SO_2-refined oil and for the same oil after a final treatment with ½ per cent. H_2SO_4 and 2 per cent. oleum :—

	Dissolution temperature. Before radiation.	After radiation.
SO_2-refined oil	65·5° C. (Previously 65·2° was found)	65·5° C.
SO_2-refined oil after final treatment with H_2SO_4 and oleum	66·8° C. (Previously 66·4° was found)	66·8° C.

Still another experiment was made, in which the crude Venezuela kerosene and the four refined products obtained therefrom were heated during 40 minutes at 180-190°, while a current of air was introduced continuously. The duration of the pre-heating was 30 minutes. It was found that the SO_2-refined oil, after a final treatment with H_2SO_4 and oleum, remained less coloured (yellow), whilst the other products had become yellow-brown or brown.[7]

Experiments with Transformer Oil.—This oil was probably of American origin (Mid-Continent). The product was treated four times with 100 per cent. SO_2 at -10° C., with continuous current :—

As mentioned above, one of the most important advantages of the extraction with SO_2 is the obtaining of two products of different chemical character, which, especially the refined oil, can be treated separately better than together. This was also proved here. The bleaching of the SO_2-refined oil with 2 per cent. "Frankonite S" on the water-bath at 90° (stirring during 20 minutes) gave an almost uncoloured product, whilst the crude distillates treated with 3 per cent. "Frankonite S" hardly bettered in colour :—

Table IV.

Experiments with Transformer Oil, probably of American Origin.

1. SO_2 treatment with 4 × 100 per cent. at −10° C., continuous current.
2. The bleaching of the SO_2-refined oil with 2 per cent. "Frankonite S" at 90° C. on the water-bath and stirring during 20 minutes. As a comparison the original crude distillate was treated under analogous circumstances with 3 per cent. "Frankonite S." The data of the refined oil, as mentioned in the table, belong to the bleached product. The refining with SO_2 gave 20 per cent. of extract and 80 per cent. of refined oil.

[7] These experiments, which were carried out by Mr. A. J. P. van der Burgh, at first served to give information about the first phenomena of decomposition, namely, formation of ultra-microscopic visible parts. In the above-mentioned case the observation of the colour was much more simple.

3. Treatment of the crude oil with 2 per cent.+5 per cent. of sulphuric acid.

	Crude distillate.	SO_2-refined oil bleached with 2% "Frankonite S."	SO_2 extract.	SO_2-refined oil after a final treatment with 2% H_2SO_4.	Crude distillate treated with 2%+5% H_2SO_4.
Sp. gr. at 15° C. ..	0·892	0·865	1·013	—	—
Colour ..	.. Pale brown after bleaching with 3% "Frankonite S."	Pale yellow.	Dark green-brown, not transparent.	—	Yellow.
Bromine number ..	2·4	2·6	1·55	—	—
Sludging value* ..	1·3	0·5	—	0·5	1·3
Dissolution temperature, with aniline, vol. 1 : 1	80·7° C.	93·0° C.	<0° C.	—	83·4° C.
Sulphur content ..	0·35%	0·12%	1·31%	0·11%	0·26%

* Sludge test after Michie; D. Holde, Kohlenwasserstoffole und Fette 6e Aufl. P. 185, Berlin, 1924.

By the SO_2 treatment the sludging value has been decreased very much, and the desulphurising also is important; a decrease of 0·23, or 65 to 66 per cent., by the treatment with SO_2 only, whereas the refining with 2 per cent.+5 per cent. of sulphuric acid causes only a decrease of 0·09, or 25 to 26 per cent. From the observed aniline point it can be concluded that the nature of the remaining hydrocarbons has changed enormously by the extraction with liquid SO_2 (an increase from 80·7 to 93·0°), while the refining with 2 per cent.+5 per cent. of sulphuric acid only augments the aniline point from 80·7 to 83·4°.

The determinations of the bromine number prove that those compounds which bind the bromine in the method of McIlhiney do not preferentially go into the extract; in each case the refined oil still has a bromine number of 2·6. This is a very important thing, because it has been proved that the "objectionable" unsaturated compounds go into the SO_2 extract,[8] while the other valuable unsaturated compounds do not, in each case, go wholly into the extract and therefore remain partly or wholly in the refined oil.[9]

We have made more analogous observations and hope to treat this subject further by the description of different researches in connection with the cracking of Edeleanu extracts of heavy oils.

The radiation during 56 hours in Uviolglass to the quartz burner caused the SO_2-refined oil to become only slightly darker in colour

[8] This is proved, *e.g.*, by the good properties of the refined oil when compared with the extract.

[9] D. Holde, "Kohlenwasserstoffole und Fette," p. 113, 1924.

(pale yellow before and dark yellow after the radiation). The aniline point of the refined oil thus treated had changed but little.

It was also found that on radiation the colour intensity of the extract decreased. At first the colour was dark green-brown, untransparent; after 56 hours, reddish and transparent; the colour of the original distillate also became brighter.

A survey of analogous and more detailed experiments on the preparation of a Californian transformer oil are found in Table V. :—

Table V. shows the great advantages of the extraction with SO_2. While not less than 17 per cent. of H_2SO_4 and 33 per cent. of oleum were necessary to give low sulphur-content, low sludge-test[10] and "Verteerungszahl."[11] a product capable of standing

TABLE V.

CALIFORNIAN TRANSFORMER OIL DISTILLATE.

(Preparation of a transformer oil with low sludging value.)

		Method without SO_2.		Method with SO_2.	
	Crude distillate.	Treated with 2%+15% H_2SO_4 (66° Bé).	Treated with 2%+15% H_2SO_4 then with 33% oleum in two portions.	SO_2-refined oil, final treatment with 2%+5% H_2SO_4.	SO_2 extract.
Yield in % of weight calculated on distillate	—	85	59	62	34
Real loss calculated on distillate on treatments with acid, alkali and on bleaching ..	—	15	41	4	—
Consumed raw material in % of weight calculated on distillate :					
SO_2	—	—	—	0·3	—
H_2SO_4 (66° Bé) ..	—	16·6	16·6	4·6	—
Oleum (20% SO_3).	—	—	33·2	—	—
NaOH	—	0·6	0·7	0·6	—
Alcohol	—	—	7	—	—
Bleaching earth ..	—	6	4·2	4·4	—
Sp. gr. at 15° C. ..	0·906	0·897	0·872	0·871	0·977
Sulphur in % by wt.	0·68	0·48	0·05	0·048	—
"Michie Test" .. (Sludge test)	—	2%	0·8	0·75	—
"Verteerungszahl"	—	0·3	0·02	0·02	—
Colour	Yellow-brown.	Yellow	Pale yellow.	Pale yellow.	Brown.

[10] See D. Holde, Kohlenwasserstofföle und Fette, p. 185, 1924.
[11] D. Holde, *l. c.* p. 184.

the same tests was obtained from the SO_2-refined oil by a final treatment with 2 per cent. + 5 per cent. of sulphuric acid. The loss of organic substance was also less, namely 41 per cent. by the H_2SO_4-oleum treatment and only 4 per cent. by the Edeleanu method. The yield of the principal products was 3 per cent. more by the SO_2 method (62 per cent.) and an additional 34 per cent. of extract was obtained.

TABLE VI.

RESEARCH ON RUSSIAN OILS.

Determination of bromine number, aniline point and radiation experiment.

	Crude distillate.	SO_2-refined oil bleached with Frankonite.	"Weiszöl" from the SO_2-refined oil.	Commercial "Weiszöl."
Sp. gr. at 15° C. ..	0·892	0·876	0·868	0·868
Colour	Dark brown, green fluorescence.	Yellow.	Water-white.	Water-white.
Bromine number, method of McIlhiney..	2·5	1·1	0·1	—
Dissolution temperature with aniline, vol. 1 : 1	79·6° C.	89·2° C.	96·6° C.	—
Colour after radiation (56 hrs.)	Has become more pale.	Dark yellow.	Very pale yellow.	Very pale yellow.

TABLE VII.

PREPARATION OF TECHNICAL "WEISZÖL" FROM A RUSSIAN DISTILLATE.

	Original distillate.	Without SO_2 Treatment with 22% H_2SO_4.	With SO_2. SO_2-refined oil after final treatment with 5% H_2SO_4.	SO_2 extract.
Yield in % of weight calculated on distillate ..	—	81	82	12
Real loss calculated on distillate	—	19	6	—
Consumed raw materials in % of weight calculated on distillate :				
SO_2	—	—	0·3	—
H_2SO_4 (66° Bé)	—	22	4	—
Oleum (20% SO_3) ..	—	—	—	—
NaOH*	—	0·5	0·4	—
Bleaching earth (Frankonite)	—	4·5	1·7	—
Sp. gr. at 15° C.	0·891	0·882	0·876	1·005
Viscosity (E) :				
At 20°	5·87	5·66	5·62	14·04
At 50°	2·07	2·03	2·04	2·6
Colour	Yellow-brown.	Water-white.	Water-white.	Yellow brown.

* Used as a solution of 18° Bé (10—11%).

EXPERIMENTS IN CONNECTION WITH THE PREPARATION OF MEDICINAL OILS AND OF TECHNICAL "WEISZÖL."—Corresponding experiments were made with an SO_2-refined oil prepared from a Russian oil; from this refined oil "Weiszöl" was obtained by treatment with sulphuric acid and 3 x 10 per cent. of oleum. A commercial "Weiszöl" product was also taken into research. The experience of the Berlin laboratory has proved that, for the preparation of this commercial product, some sulphuric acid and 5 x 10 per cent. of oleum is necessary.

TABLE VIII.

PREPARATION OF A MEDICINAL OIL FROM A HEAVY CALIFORNIAN DISTILLATE

		Without SO_2.	With SO_2.	
	Original distillate.	Treatment with H_2SO_4 and oleum.	SO_2-refined oil after final treatment with H_2SO_4 and oleum.	SO_2 extract.
Yield in % of weight calculated on distillate ..	—	30	32	36
Real loss calculated on distillate	—	70	32	—
Consumed raw materials in % of weight calculated on distillate :				
SO_2	—	—	0·3	—
H_2SO_4 (66° Bé)	—	2	1·3	—
Oleum (20% SO_3) ..	—	70	35·5	—
NaOH	—	0·5	0·3	—
Alcohol	—	5·0	3·0	—
Bleaching earth (Frankonite)	—	4·8	5·0	—
Sp. gr. at 15° C.	0·947	0·887	0·887	1·019
Viscosity at 50° C. ..	9·33	4·63	4·70	50° = ca 20 100° = 2·1
Quality test*	—	Wholly stand the quality tests of the Ph. G. V.		—
Colour	Dark brown.	Water-white, not fluorescent	Water-white, not fluorescent	Dark brown.

* Here the German tests were taken into account.

In Table VI. some observations are united. The "Weiszöl" obtained from the SO_2-refined oil had a bromine number (addition) of practically 0. The aniline point of this product was high, and it was completely colourless, just as the commercial product which served for comparison.

The radiation for both products, after 56 hours, gave but a very pale yellow colour. After this radiation, the aniline point of the laboratory "Weiszöl" had not changed (96·8° C. before and after radiation).

In Tables VII. and VIII. are found the details of the preparation, yield and properties of technical "Weiszöl" obtained from a Russian distillate, and of medicinal oil from a heavy Californian distillate. These details also prove that the SO_2 method gives very good end products, with an important economical use of raw materials, and even a higher yield of the end products. Extract is also produced.

SO_2 will also find important application in refining vegetable and animal oils and fats. Thus it will be possible to accumulate on one side the compounds with a more saturated character, and on the other the strong unsaturated glycerides. The latter will show in a more pronounced way their specific properties, which are connected with their unsaturation, and this is of importance for special technical applications.

It is possible to extract with liquid SO_2 the smell- and taste-causing substances from rape oil, and thus obtain the character of an edible oil. Still better than to the glycerides, the SO_2 extraction can be applied to the free fatty acids, because the fats contain also mixed glycerides.

The Valuation of Motor Spirit and Lubricating Oils.*

By HAROLD MOORE, M.Sc. (Tech.), A.I.C., F.C.S.

IN valuing lubricating oils it is essential to base the valuation upon experience of similar oils originating from the same crude. The analysis should be used largely as an indication of the origin of the product. The minimum number of tests essential for commercial valuation of lubricants are :—

Specific gravity, Viscosity at 70° F., 100° F., 140° F. and 200° F., cold test, flash point, coke test and appearance.

Gravity.—This is no direct indication of the suitability or behaviour of an oil, but is an indication of its origin. For example, medium viscosity lubricating oil of 60 seconds at 200° F. Redwood if of Pennsylvanian base would have a gravity of 0·880-900 ; if Texas or Californian the gravity would be 0·925-940 ; if of Russian origin, the gravity would be 0·910-920. Commercial grades are generally blends containing two or more components which may originate from different fields. The specific gravity given by blends may be calculated from the arithmetical proportion of the constituents.

Flash Point gives little direct indication, as it is so liable to be influenced by contamination. High flash point is an indication of close fractionation in refining processes. Pennsylvanian oils have higher flash points than other oils of similar viscosity.

Viscosity.—In the valuation of viscosity one must bear in mind that the empirical readings of instruments such as Redwood, Saybolt, Engler and Barbey, are not direct functions of absolute viscosity. For example, in the Redwood instrument an oil of 60 seconds is not twice as thick as an oil of 30 seconds, as the instrument is so constructed that a substance absolutely devoid of viscosity would give a reading of about 26 seconds. It is advisable to determine viscosity over a range of temperatures, when the results can be plotted in the form of graphs reading viscosity against temperature. Motor oils vary from 90-300 seconds Redwood at 140° F. It is difficult to decide exactly the viscosity required for lubrication of any particular vehicle. As a result, oil blenders frequently issue recommendation charts stating the type of oil which they recommend for each vehicle, the actual viscosities most suitable for the purpose being determined by experience. The following rule acts as a rough guide of the viscosity most suitable for any particular engine.

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* Paper read before the Commercial Motor Users' Association at Olympia on Thursday, November 5th, 1925.

Vehicles possessing large engines working at comparatively low loads operate satisfactorily on thin oils. Small engines working on heavy loads require thicker oils. Old vehicles whose pistons and piston rings are heavily worn are best suited by using thick oils, which have the effect of bridging comparatively large piston clearances and passing comparatively slowly along the cylinder walls into the combustion space. Where thin oils are used on old engines possessing large piston clearances and worn piston rings, the consumption of lubricant becomes excessive.

Apart from considerations of load factor, the actual size of the engine has comparatively little effect. Extremely thin oils give noisy running and excessive consumption of lubricant. Oils of excessively high viscosity give low mechanical efficiency—a point indicated by sluggish running of the engine, particularly when not fully warmed up. When viscosity-temperature curves are prepared, the inclination of these curves is dependent upon the base of the oil employed. Pennsylvanian oils do not show such a large falling off in viscosity with rise in temperature as do those of Texas or Californian origin. Russian oils are intermediate in the inclination of the viscosity-temperature curve. Typical light motor oils of three origins possessing approximately the same viscosity at 200° give the following readings :—

Test.	Pennsylvanian.	Russian.	Californian
Gravity	0·881	0·911	0·935
Closed Flash Point	420° F.	384° F.	372° F.
Viscosity at 70° F., Redwood ..	690	1120	1392
Viscosity at 100° F., Redwood ..	268	355	392
Viscosity at 140° F., Redwood ..	108	121	121
Viscosity at 200° F., Redwood ..	51	52	50

The heavier motor oils are generally prepared by blending viscous filtered residual oils with the more mobile (thinner) distillates. As the majority of cylinder oils are prepared from Pennsylvanian or Mid-Continental crude oils, the result is that the heavier blends are almost invariably mixtures containing at least two different bases. For example :—

	Wholly Pennsylvanian.	Russian and Mid-Continental Base.	Californian and Mid-Continental Base.
Gravity	0·890	0·902	0·925
Closed Flash Point	422° F.	390° F.	375° F.
Viscosity at 70° F., Redwood ..	1985	2700	3620
Viscosity at 100° F., Redwood ..	690	901	925
Viscosity at 140° F., Redwood ..	239	275	280
Viscosity at 200° F., Redwood ..	80	80	80

The Mid-Continental type of oil is found in the field centered in Oklahoma and extending between North Texas and Kansas. The oils in this field are not generally considered quite as high-

class as the Pennsylvanian types, although possessing very much the same characteristics and closely related chemically. There is no doubt that, given other properties as equal, the flatter viscosity curve of the Pennsylvanian oils is a distinct advantage, and one must recognise that this is generally accepted by the world's oil market, as both Pennsylvanian crude and Pennsylvanian lubricating fractions command considerably higher prices than those obtained from other fields. The oils used for motor lubrication vary between viscosities of about 50 seconds at 200° F. to approximately 100 seconds at 200° F. The lighter oils are used almost exclusively for light American cars, while heavier oils of 100 seconds at 200° F. form the heavier end of the range employed on commercial vehicles.

Cold Test.—High cold test is a disadvantage and occasionally may cause injury to bearings through the oil being solid when the engine is started up. Such occurrences are comparatively rare, but it is fairly common to encounter difficulty in starting owing to extremely high viscosity of oils when at temperatures only slightly in excess of the cold test. High cold test is brought about by the presence of paraffin, which at low temperatures falls from solution and causes solidification. As both Russian and asphaltic oils are practically free from wax, the freezing point is much lower than the temperatures encountered in motor lubrication, and these oils give no difficulty on account of this property. Mid-Continental and Pennsylvanian oils are wax-containing, and unless the paraffin wax is effectively removed their high cold test may cause trouble. In oils of Pennsylvanian origin the wax is generally efficiently removed, but some of the Mid-Continental oils used for blending purposes contain quite a quantity of wax, and it is fairly common to meet high cold tests in oils which are blended off Russian or asphaltic base oils together with Mid-Continental base stocks. The highest cold test encountered in this country is in the neighbourhood of 50° F., but figures as high as this are not satisfactory. A reasonable limit for use is 45° F. for summer and 35° F. for winter. In the past it was rare to meet Pennsylvanian oils with lower cold test than 30° F., but during the last few years improved wax extraction processes have been employed in the United States, and it is possible to get Pennsylvanian motor oils with cold tests below 20° F.

Coke Test.—Assuming that a given amount of oil passes the piston, the amount of carbon formed will be roughly proportional to the coke value of the oil. As the amount of oil passed is dependent upon the viscosity, it does not follow that large amounts of carbon deposit are always the result of using an oil of high coke value. Usually the thinner oils possess lower coke values.

Appearance.—In oils of identical or similar class made from the same raw material, the lighter the colour the better the oil, but such a direct interpretation is generally complicated by the fact that the majority of oils are mixtures of various products. In pale oils (yellow to transmitted light), red oils (red to transmitted light) a blue fluorescence indicates asphaltic or Russian origin. A greenish fluorescence indicates Pennsylvanian origin. A green colour to reflected light, generally accompanied by a red appearance to transmitted light, indicates the presence of filtered residual oils. The clearness to transmitted light is an indication of good refining, and cloudiness is undesirable.

Compounded Oils.—Animal and vegetable oils are not so stable as mineral oils, particularly on account of their liability to oxidise, but they possess the property of maintaining a film when subjected to extreme pressure in a bearing. In this respect they are superior to mineral oils. The advantage of a small proportion (2 per cent.—10 per cent.) of animal or vegetable oil to mineral oil will give the resulting product this particular property. The main oils used for blending are lard oil, coconut oil, tallow oil, rape oil, sperm oil, and neatsfoot oil. Castor oil is not often used for compounding purposes on account of its comparative insolubility in mineral oils, although it is occasionally used in practically pure form for racing purposes.

Regarding the comparative value of oils of various origin in the past and probably at the present, the majority of oil technologists prefer low gravity oils, but during recent years the use of Texas and Californian oils has been steadily increasing and they are giving excellent results in the majority of cases. Russian oils have always held a good reputation as lubricants for internal-combustion engines.

There is every indication that Persian oils would prove good lubricants. The variation in retail prices of motor oils is undoubtedly largely due to the cost of packages and to the cost of handling and advertisement. The author's experience has been that price is no criterion of the suitability of an oil for any particular work, nor even of the value of the constituents which it may contain, the higher priced oils frequently being of the poorest quality and being made from the cheapest raw materials.

The Valuation of Motor Spirit.

Assuming that one has to limit one's self to a comparatively small number of tests in order to minimise expense and avoid delay in obtaining results, it is recommended that the number of tests should be limited to the following:—Specific Gravity, Engler Distillation, Corrosion Test and Aniline Cloud Test.

Specific gravity is of importance in that the weight of spirit (by volume measure) varies in direct proportion to the specific gravity. The variation in heat values of various spirits on a weight basis is not so great as the difference in the specific gravity. Therefore one finds in practice the higher the specific gravity the greater the power obtainable per unit volume of spirit.

Engler Distillation.—Distillation range is of great importance in the valuation of spirit. It decides ease of starting, flexibility, and to a smaller extent the tendency to detonation. The ease of starting is determined by the amount of spirit which distils over at the lower temperatures between Initial Boiling Point and the region of 100° C. Low Initial Boiling Point may assist preliminary starting, but experience has indicated that for ready warming up and taking load it is necessary to have a fairly large proportion of the spirit distilled before the temperature of 100° C. The amount distillable at various temperatures above 100 °C., together with the amount at 100° C. gives a demonstration of the flexibility. High end point is not desirable, and close distillation ranges tend to give flexibility. The proportion over at 175° C. or the temperature at which 90 per cent. has gone over is a better indication of value than the actual end point.

Corrosion Test.—With well refined spirits the amount of gummy deposit left in the corrosion test is too small to be either weighed or observed, but when the deposit weighs more than 0·2 g. per 100 c.c. spirit, the effect on an engine becomes distinctly noticeable. Smaller quantities, of course, possess an effect, but are not so serious. When dealing with spirits from known suppliers, it is not always necessary to make this test, as one can safely assume that the product has been well refined.

Aniline Cloud Test.—The best method of determining tendency to detonation is to actually test the spirit in an engine—preferably one so designed as to allow variation in the compression ratio. As this test is comparatively expensive, the aniline cloud test may be used as a rough measure of the tendency to detonation. The aniline cloud test is a measure of the percentage of aromatic hydrocarbons present, but is also an indication of the presence of naphthenes and unsaturated compounds.

Anti-Detonators.—Although hitherto no really satisfactory anti-detonator has been found, the use of tetraethyl lead has met with a certain amount of success in the United States. Its use at present has been held up on account of the poisonous nature of the substance. It is quite possible that ethyl alcohol may come into use at any time as an anti-detonator, and it is probable that this fuel will enter the market as an anti-detonator rather than as a fuel for use in the pure state.

The Refining of Mineral Oils.*

By H. I. Waterman, Ph.D.

Our aim in refining petroleum distillates is to improve their qualities. To effect this improvement is extraordinarily difficult because it often concerns many properties having no connection with one another. Among other things it falls to us to remove substances which give to the products a colour or disagreeable odour, bodies which under the influence of light and/or air become dark or lead to the separation of gummy substances. In special cases it is desired to eliminate a known group of hydrocarbons, the aromatic bodies for example, as occurs in connection with kerosene refining. In still other circumstances it is proposed to remove as far as possible all the sulphur compounds. When it arises that we are dealing, not with those petroleum distillates which are to be transformed chemically—and hence consumed—such as petrol, kerosene, gas oil or fuel oil, but with distillates, which will retain their nature wholly or in part during use, such as lubricating or transformer oils, we demand especially products which are able to resist contact with the air and relatively high temperatures without too much decomposition (formation of carbon or asphalt).

In certain cases the presence of sulphur (or a halogen) facilitates the separation of dark bodies, frequently in such a manner as to give the impression that carbonisation is taking place. Hence with many distillates such as benzine, kerosene, lubricating oil and others of a similar nature it is desirable to remove as far as possible sulphur or halogens[1] before the oil is sold. It is a well-known fact that oxygen or air also favours the formation of asphalt in petroleum distillates. In the examination of a low boiling distillate obtained by cracking gas oil in a retort, it is said that the action of bromine, even ice cold, on the highly unsaturated product obtained is to give bromine compounds which on distillation at as low a temperature as 100° C. [2] give considerable separation of carbon. In their classic research on the action of temperature and pressure on the paraffins. T. E. Thorpe and J. Young[3] observed that the action of bromine on certain fractions of their reaction product gave rise

* Read before the 5th Congress of the Chimie Industrielle, Paris, October, 1925. (Translated from the French by S. W. Adey.)

[1] It is mainly chlorine which is of importance from this point of view, since methods of refining, such as that of Dunstan, when carelessly applied can lead to chlorinated products.

[2] An observation of Messrs. J. N. J. Perquin and L. W. H. Borgesius.

[3] Ann. **165** 14 (1873).

to a dark coloration and the deposit of a "tarry mass" at the bottom of the flask.

F. J. Nellensteyn also, by the action of iodine on unsaturated hydrocarbons has obtained a separation of carbon which firmly retained the iodine.[4] In a communication by the Silica-gel Corporation[5] it is stated that while the presence of sulphur in kerosene adds considerably to the carbonisation, unsaturated bodies are not so harmful as was thought. In the bulletin in question, the conclusion arrived at in a certain instance is, "it is only necessary to effect the removal of the sulphur compounds to obtain an oil of fine burning quality, even though the percentage of unsaturated hydrocarbons is but slightly reduced."

The Silica-gel Corporation even believes that the presence of sulphur in benzine or lubricating oils promotes the formation of carbon deposit in the cylinders of internal combustion engines. In many of the experiments which we have undertaken we have, in fact, observed that the presence of free or combined sulphur has a bad influence on the quality of kerosene by causing it to burn with a smoky flame (see table below). The quantity of soot deposited on the lamp glass was estimated by eye and expressed numerically (10 representing the greatest quantity). It is seen from the tables that not only sulphur but also halogen compounds, in our case ethyl bromide, can lead to a deposit of soot being formed.

No.			Deposit of soot on lamp glass after six hours.
1	250 c.cs.	of commercial kerosene	1
2	„	+1 vol. % (*i.e.*, 2·5 c.cs.) of $(C_2H_5)_2S$	10
3	+5 vol. %	(*i.e.*, 12·5 c.cs.) of $(C_2H_5)_2S$	10
4	„	+1·7 c.cs. C_2H_5HS	8
5	+8·6 c.cs.	C^2H^5HS	8
6	„	saturated with sulphur in the cold (·6% S.)	8
7	„	without any addition	1
8	„	+3·44 c.cs. C_2H_5Br	7
9	„	+17·2 c.cs. C_2H_5Br	7
10	„	+3·73 c.cs. C_2H_5I	0
11	„	+18·6 c.cs. C_2H_5I	0
12	„	without any addition	1
13	„	+16·3 c.cs. C_2H_5Cl	1
14	„	+12·7 c.cs. $C_2H_5Cl_3$	1
15	250 c.cs.	without addition	1
16	„	into which chlorine had been passed	Formation of soot, but after some time the wick and the light went out.

[4] F. J. Nellensteyn, Chem. Weekbl. **21**, 102 (1924).

[5] The Silica-gel Corporation, Baltimore. The refining and recovery of petroleum products with silica-gel, Bulletin No. 4, July, 1923.

At least the experiments confirm the fact that the presence of sulphur favours considerably the formation of free carbon.

Unfortunately the wicks used in these experiments were made of organic material, a defect, which while not affecting the technical significance of the results could have well been avoided by employing glass wool.

Another experiment which we have carried out[6] in this connection is as follows. Three Carius tubes were heated to 240° C. for two days, the first containing diethyl sulphide, the second the same kerosene as in the last experiment, the third a mixture of equal volumes of diethyl sulphide and the kerosene. After cooling it was noted that the first tube was practically uncoloured, the second was a clear brown and the third a deep brown. The same kerosene was vigorously attacked by chlorine, even at room temperature, with the evolution of hydrochloric acid. Chlorine was passed continuously through the liquid and at the end of two days it remained colourless, but had become very viscous. After two days more, however, it became coloured, brown by reflected light and violet by transmitted light, but cleared on standing. When this solution was heated to within a few degrees of its boiling point it commenced by taking on a green colour, then it became brown and finally black. Two days later, the whole mass having become quite cold, it had the consistency of asphalt. Extraction with a low boiling benzine gave a residue of carbon.

As we see this carbonisation takes place easily, even at low temperatures, and may have considerable effect upon the results of our halogen value determinations.

Before taking further account of this formation of asphalt industrially, one should consider the presence of sulphur or sulphur compounds in petroleum distillates in so far as they give rise to a disagreeable odour and to SO_2 and SO_3 on combustion. In connection with these two gases it should be noted that petroleum technologists maintain that there is no fear of their attacking metal parts of engines, in fact it is well known that boilers burning highly sulphurous residues show no ill effects. The only danger of corrosion occurs when the temperature is sufficiently low to permit of the formation of water. Nevertheless in practice reasonable desulpurization of benzine and kerosene is always demanded.

It is clear that the composition of the crude is not the sole determining factor in the nature of the products of distillation. The method of distillation itself has a great influence, in that it is always more or less destructive in nature, leading to the formation of highly unsaturated bodies, themselves unstable. As an example

[6] The work of M. Kortlandt.

I may cite a certain paraffin wax[7], whose m.p., according to the method of Shukoff was 50·6° C., and bromine number (this substance had been added) determined by addition according to McIlhiney's method was 0·5. The fully saturated product was submitted to cracking at 450° under the following conditions:—

(*a*) The gas formed was removed and the pressure in the vessel maintained at 7 atmospheres.

(*b*) The pressure was allowed to increase to 49·5 atm. by the formation of gas.

(*c*) Decomposition was permitted in the presence of hydrogen under high pressure (Bergius) (i.) Init. press.=60 atm. Max.=142 atm. (ii.) Init. press.=110 atm. Max.=219 atm. the gaseous products of reaction not being removed.

The lower the pressure employed in the above experiments[8] the higher the degree of unsaturation of the liquid products obtained.

Product of exp.	(*a*)	Bromine no. (addition)	..	63·2	
,, ,,	(*b*)	,, ,, ,,	..	28·7	
,, ,,	(*c*)	,, ,, ,,	..	22·1 21·1	60 atm. initial press.
		,, ,, ,,	..	14·5	110 atm. initial press.

The experiments carried out under strictly comparable conditions show definitely that the nature of the products obtained during distillation will depend, apart from the nature of the crude, on the method of distillation employed. Hence, in so far as distillation results not only in the physical separation of the various fractions, but also in decomposition of some of the hydrocarbons or other bodies, thus far will it place certain limitations upon the chemical treatment which the oil must finally receive.

What we have just said concerns not only the hydrocarbons but also the suphur compounds. It is a well-known fact that many distillation processes, carried out without the desire to cause cracking, on oils of high sulphur content such as Mexican crude, lead to the evolution of large volumes of sulphuretted hydrogen. Here again the method of distillation will have considerable influence upon the nature and amount of sulphur compounds present in the various fractions.

[7] To give an idea of the ultimate composition of paraffin, I may say that an analysis of Rangoon paraffin gave H=14·9%, C=85·2%. A previous publication by H. I. Waterman and J. N. J. Perquin, Versl. Kon. Akad. v. Wetenach XXIV. 259 (1925) gives H=14·8%, C=84·6%. The latter analysis is the more correct. See also a communication by W. J. Wilson, Journ. Inst. Petroleum Technologists, **11**, 60 (1925), which gives for the analysis of a Rangoon paraffin melting at 58° C., H=14·75%, C=85·25%.

[8] H. I. Waterman and J. N. J. Perquin, Proc. Kon. Akad. v. Wetensch, Amsterdam, XXVI., Nos. 3 and 4 (1924), p. 226; XXVII., Nos. 1 and 2 (1924), p. 132.

Another difficulty which crops up is that, to tell the truth one is not always sure to what standards of testing one should work. True enough, methods of testing petroleum products have been standardised[9], but one is not always aware of the real significance of the various tests, e.g., what is the real use of the Doctor Test or the Corrosion Test and what value attaches to the determination of degree of unsaturation of benzine (vide p. 86 of the American publication mentioned).

Without doubt this standardisation of testing is highly advantageous in that it enables us to produce uniform products, but what is more important is that we should search for the relations which these tests bear to the actual economic value of our products. Not long ago, in fact, Brooks[10] showed that the olefines, often removed in refining ought to be considered in certain cases as amongst the most valuable constituents of the oil.

The last fact clearly shows how necessary it is becoming that we should attempt a really complete analysis of these hydrocarbon mixtures, quite a possibility as far as the lowest fractions are concerned. We should then be able to base our choice of a method of refining upon this analysis, or in other words we ought to know exactly how each of the hydrocarbons or other bodies found in the mixture will behave during refining.

Here we have a work of such magnitude that it would be furthered better, I think, by international co-operation. It would be necessary then to nominate an international commission, whose duty it would be to study the influence of these various factors.

As an example of the processes of refining I have chosen amongst others, that of Edeleanu.[11] The value of this method lies mainly in the fact that it enables us to separate, by a simple extraction with liquid SO_2, involving negligible loss, the products of a petroleum distillation, such that they are divided into two parts, each possessing different chemical properties and so enabling each to receive a suitable final refining.

It is important to note that liquid SO_2 possesses great desulphurizing power.

A paper entitled, "The Importance of the Edeleanu Process," by the author and J. N. J. Perquin, appearing in this journal, page 560, gives the results of investigations carried out in collaboration with Dr. A. Lazor and his colleagues.

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[9] E.g., see "Specification for petroleum products and methods for testing. Technical paper 323, Bureau of Mines, Washington, 1923," and "Standard Methods of Testing Petroleum and Its Products," Inst. of Pet. Technologists, London, 1924.

[10] B. T. Brooks, Chem. and Met. Eng., **24**, 1022 (1921).

[11] Edeleanu, z.f. angew. Chem. **36**, 573 (1923).

The Silica-gel and Dunstan hypochlorite methods owe their value mainly to their desulphurizing powers which are very considerable and compare with that of the Edeleanu process.

In the case of a certain petroleum fraction of sp. gr. 0·86–0·92, obtained from Persia, a 20 per cent. reduction in sulphur content was obtained using 54 per cent. of silica gel in two treatments (28 per cent. and 26 per cent. respectively). Using a Mexican kerosene, in one experiment 117 per cent. of gel by weight gave a reduction in sulphur of 60–70 per cent., in another and using 114 per cent. by weight of gel, the reduction was about 50 per cent. For the above experiment the gel was made in our own laboratory, but with a view to forming a comparison we have carried out tests using the commercial product. This was a very fine brownish grey powder, which before being used was heated to 150–250° C. in an electric furnace with a plentiful supply of air, until all the water vapour had been driven off, when it was allowed to cool in a desiccator. A c.c. of Mexican kerosene (S=1·75 per cent.) were agitated each time with a/5 grams of gel for two hours. Four successive agitations were carried out.

	Crude kerosene.	After 1st treatment.	After 2nd treatment.	After 3rd treatment.	After 4th treatment.
Sulphur content ..	1·75%	1·37%	1·09%	0·86%	0·65%
Colour	Deep red brown	reddish brown	yellowish brown	yellow	lighter yellow.

Thus, using 4a/5 grams of gel a drop in sulphur content of 1·1 per cent. was obtained, *i.e.*, a full 60 per cent. reduction, a result just slightly better than that obtained with our own silica-gel. It will be observed that silica gel also possesses great decolorising power.

The Dunstan Hypochlorite Process. In this process—which employs a hypochlorite solution it is very important carefully to regulate the quantity of free alkali present.[12]

In the course of various tests carried out on distillation products of Mexican petroleum[13] varying in sp. gr. from ·84 to ·92, we have observed a 68–40 per cent. reduction in sulphur content, employing let it be noted, a final filtration through bauxite. Without the additional bauxite treatment, the desulphurization does not exceed 42–27 per cent.

In another test, carried out by M. Boagers, using only the Dunstan hypochlorite method, and omitting the bauxite, on a

[12] A. E. Dunstan, The Hypochlorite Process, J.I.P.T. **10**, No. 42 (April, 1924).

[13] H. I. Waterman and J. H. Heimel, J.I.P.T., **10**, 812 (1924).

Mexican kerosene of sp. gr. 0·815, the following results were obtained:

Mexican kerosene of sp. gr. 0·815 and S. content	= 1·08%
After first soda wash	= 1·04%
After first hypochlorite wash	= ·89%
After second hypochlorite wash	= ·75%
After second soda wash and a water wash	= ·72%

Conclusion.

I trust that I have shown by these few examples borrowed from the field of mineral oil refining that to be able to select, apply and reap the full benefit of distillation and refining methods it is essential:—(*a*) To know the nature of the oil in question, *i.e.*, it should be known what groups of compounds it contains. It is not sufficient to be aware that the distillate consists almost entirely of paraffin, is rich in aromatics or has a high percentage of olefines; it is desirable that one should be acquainted, to some extent, with the percentage of these hydrocarbons or groups of hydrocarbons present. (*b*) To know how the process of refining under consideration will behave towards each of the bodies present, and should distillation result in any decomposition, to what extent and in what manner this decomposition will take place.

In England successful work in this direction has been carried out mainly by Dunstan and his collaborators. (*c*) To know exactly the nature and proportion of those bodies or groups of bodies which should and can be made to exist in the final product.

The problem of refining can only be solved by systematic scientific study and it seems to me that international scientific co-operation constitutes the most rapid means of attaining this end.

The Action of Sulphuric Acid on Cracked Spirit.

By C. M. Houghton and S. Bowman.

It is now a generally accepted fact that the behaviour of a motor spirit in the modern automobile engine is largely a function of the chemical nature of that spirit; that is to say, ease in starting and the highest useful compression that can be employed depend on the relative proportions of paraffin, aromatic or naphthenic hydrocarbons present.

To these three groups it is certain that in the near future a fourth group of unsaturated hydrocarbons must be added due to the introduction of cracked spirit, the term "unsaturated" being employed here to denote those compounds containing one or more double bonds. Now, apart from the fact that this group is liable to contain comparatively unstable gum-forming constituents, whose determination is necessary, its removal is essential before determination of the other three groups can be attempted.

With regard to the determination of the paraffin, aromatic and naphthene content of a spirit a number of methods are available based on the work of Chavanne and Simon[1], Tizard and Marshall[2], Thole[3], Hoyte[4] and Ormandy and Craven[5], but it should be noted that the paraffin content, being taken by difference, is dependent on the accuracy of the determination of the other hydrocarbons.

In all these methods the determination is based on the difference in certain characteristics before and after treatment with sulphuric acid of 98–100 per cent. strength, it being assumed that under the conditions of this treatment only aromatic hydrocarbons are removed. If, however, other hydrocarbons are present—e.g., unsaturates, which are also attacked by the acid wash, those characteristics, whether they are the critical temperature of solution in aniline, specific gravity or refractive index, will be vitiated to a corresponding extent. It is therefore necessary that such hydro-

[1] *Comptes Rend.*, 1919.
[2] *J. Soc. Chem. Ind.*, 1921, 20T.
[3] *J. Soc. Chem. Ind.*, 1919, 39T.
[4] *J. Inst. Pet. Tech.*, 1925, 76.
[5] *Ibid.*, 1924, 101.

carbons be removed in the first place, and if the means of removal can be made an index of the proportion present so much the better.

It is well known that sulphuric acid of moderate concentration has a selective solvent action on unsaturated hydrocarbons, and Dunstan[6] has suggested 80 per cent. acid for this purpose. Brookes and Humphrey[7] have studied the action of this reagent on the simpler olefines and diolefines, and find that the lower mono olefines are completely soluble, forming secondary and tertiary alcohols and esters with a tendency to polymerise with increasing molecular weight. Tars are formed with diolefines, and in each case the polymers are partially soluble in the residual oil.

The following experiments had for their object the determination of the strength of sulphuric acid, most effective in producing polymerisation of olefines in cracked spirit.

The method used was in general as follows:—

A 100 c.c. sample of spirit is distilled and its final boiling-point noted, and the amount of reflux from the column into the distillation flask on removing the flame is measured. A further 100 c.c. sample of the spirit is treated with acid, the decrease in its volume is noted, and it is then distilled in the same way as the original spirit *up to the final boiling-point of the original.* The volume remaining in the flask is measured, and it is tentatively assumed that the difference between this volume and that of the reflux using the original spirit is a measure of the polymerisation that has occurred. All the treatments were carried out in a 300 c.c. separating funnel and the distillations with a 150 c.c. flask fitted with a four-pear still-head.

The cracked material used was obtained from vapour-phase cracking of gas oil and would naturally contain a high percentage of unsaturates, and was in fact entirely soluble in 95 per cent. sulphuric acid. It was diluted with aviation spirit (or a fraction distilled therefrom), which was taken to be entirely saturated as there was no appreciable diminution in volume and no rise in its F.B.P. on prolonged shaking with 95 per cent. H_2SO_4.

1st Series of Experiments.

A quantity of the cracked spirit was distilled through a 12-pear column and the fraction to 100° C. collected. This formed 65 per cent. of the original and had S.G. 0·8335 at 60° F.

Aviation spirit was treated in the same way, a fraction having S.G. 0·6895 at 60° F. being obtained.

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[6] *Ibid.*, 1918.
[7] *J. Amer. Chem. Soc.*, 1918.

The two distillates were mixed in the ratio of one part by volume of the cracked to four parts by volume of the straight spirit.

The mixture had F.B.P. 108° C., and on removing the flame 2 c.c. of liquid collected in the flask.

The mixture was treated with acids of 95, 92·5, 90, 87·5 and 85 per cent. strength. The time of shaking was five minutes and the quantity of acid was 50 c.c. It was found that results could be repeated consistently.

It was observed during this series of experiments that the residue after distilling the treated spirit was greenish blue and that this colour was not destroyed by either water or soda. Also that with the lower-strength acids a small quantity of viscous tar intermediate in density between the spirit and the acid and miscible with neither was produced.

The results were as follows:—

Acid strength.	Reduction in volume of spirit.	Increase in residue at 108°.
% H_2SO_4	c.c.	c.c.
95·0	13·0	4·5
92·5	7·0	6·0
90·0	6·0	6·0
87·5	7·5	2·5
85·0	5·0	1·0

The sharp drop in the reduction in volume between 95 and 92·5 per cent. acid probably indicates the neighbourhood of minimum strength for solution of aromatics (undoubtedly present in the spirit). The interesting point is, however, the indication of a maximum rise in high-boiling fractions with acid of about 91 per cent.

2nd Series of Experiments.

Instead of the low-boiling fractions only, the original cracked spirit (S.G. 0·839) was mixed with aviation spirit in the same ratio as before. In view of the greater tendency of high-boiling olefines to polymerise the effect should be of greater magnitude than in the previous experiments. A heavier acid treatment was given—two washes, each of 50 c.c. acid, agitated for ten minutes. The acids used were as before with the addition of 91 per cent.

The F.B.P. of the spirit used was 144° C. and distillations were taken up to this point. The residue collecting in the flask at the F.B.P. was again 2 c.c. for the untreated spirit, and this was subtracted from the residues at 144° C. of the treated spirits.

The results were as follows:—

Acid strength.	Reduction in volume of spirit.	Increase in residue.
% H_2SO_4	c.c.	c.c.
95·0	20·0	3·0
92·5	11·5	7·0
91·0	10·0	7·5
90·0	8·5	7·0
87·5	7·5	5·0
85·0	7·5	5·0

These results are of the same general character as those in the first series, indicating that in so far as polymerisation can be measured by the method used, 91 per cent. seems to be the optimum strength of acid for producing polymerisation in spirit of the class used here.

Experiments are being continued using mixtures of the cracked and straight-run spirit in different proportions, and also to ascertain the effect of this strength of acid on aromatic hydrocarbons.

Our thanks are due to Dr. Dunstan, on whose suggestion this work was carried out, and to the Anglo-Persian Oil Co. for permission to publish these results.

Investigation of the Composition of Cracked Spirit.

HAROLD MOORE, M.Sc. (Tech.), A.I.C., F.C.S., and R. B. HOBSON, A.M.C.T.

IN view of the interest which has been recently attached to the composition of cracked spirit and of the importance of obtaining some method of co-relating the chemical composition and the tendency to detonate, it has been decided to publish the following notes describing some experiments made on cracked spirit produced in a Cross Cracking Unit. This plant is operating on a refined kerosene originating from the Russian field, which probably accounts for the high naphthene content of the product. The spirit used for these investigations was supplied by the Medway Oil and Storage Co., and consisted of the distillate from a Cross Unit after a very slight acid and soda refining treatment. The spirit is being put on the market in large quantities and the nature of the refining has been sufficient to give entirely satisfactory results in practice.

The spirit, on being tested, gave the following results :—

Sp. gr...	0·748 @	15° C.
Engler Distillation (I.P.T.)—		
Initial boiling point		34° C.
	2% @	50° C.
	9% @	75° C.
	24% @	100° C.
	51% @	125° C.
	87% @	150° C.
Final boiling point		167° C.
Total distillate	97%	
Residue in flask	2%	
Loss	1%	

The method of procedure employed for determining the base hydrocarbons in these investigations was to fractionate the spirit into four fractions, the temperature limits of the fractions being those recommended by the Institution of Petroleum Technologists, namely, those boiling up to 95°C, 95°–122°C, 122°–150°C and the

residue remaining at 150°C. The mean molecular weight of the monolefines was calculated from the percentage of fractions distilling from these limits. It was assumed that the mean molecular weight of the monolefines over the four fractions was 91, 105, 119 and 140 respectively, the latter figure being estimated after an examination of the distillation range of the products. The original product was examined for iodine value by Wijs method as described by Ratcliffe and Polychronis, Journal of the Society of Chemical Industry, 31st March, 1916, which has been found by the authors to be very satisfactory on both light and heavy petroleum distillates. The iodine value of the spirit was found to be 56·3 and on estimation based on the mean molecular weight of the monolefines present (which could be obtained by calculation from the percentages of distillate collected in the above mentioned fractions) yielded a figure for unsaturated content of 24.9%. The naphthene estimation was based upon the aniline cloud point of the spirit after sulphonation with 98 per cent. sulphuric acid, taking into consideration the boiling point of the spirit and employing the factors based upon the experiments of Mr Ricardo given in the Journal of the Institution of Petroleum Technologists, December 1922. The naphthene content obtained from the aniline cloud point of the unfractionated spirit was calculated to be 47·7%. In order to determine the aromatic compounds present it was first necessary to eliminate the olefines by washing with 80% sulphuric acid. The authors had however, some doubt as to whether a clean cut could be obtained by the use of 80 per cent. acid, *i.e.*, whether 80 per cent. acid would satisfactorily remove the olefines without affecting the aromatics. Experiments were therefore made with 80 per cent. sulphuric acid washes, the period of washing and the volume of acid used being varied. The completeness of olefine removal was decided by determining the iodine value of the product after washing. In the first place, three volumes of 80 per cent. acid were employed. As it was thought that the removal was not complete, a further six volumes were employed before the iodine value was determined. After this second treatment it was found by the iodine value that only 32·5 per cent. of unsaturated compounds present had been removed. Therefore, the washing was further continued and another six volumes (making 15 volumes in all) were used, the period of washing being increased to 72 hours. The product from this washing gave an iodine value of 25·3.

A further washing with 3 volumes of acid for 24 hours made no difference to the result, indicating that an equilibrium had been reached when approximately 55 per cent. of the olefines had been extracted. It was therefore decided to increase the strength of acid until a minimum strength was obtainable at which the unsaturated

compounds were completely removed. The following data gives the steps taken to arrive at this point:—

Acid washings.	Period of washings.	Iodine value.	Aniline cloud point, °C.	% of unsaturated compounds present removed.
3 volumes 80% strength acid	24 hrs.	—	47·1	—
Further 6 volumes ..	Further 24 hrs.	38·0	—	32·5
„ 6 „ ..	„ 73 „	25·3	48·7	55·0
„ 3 „ ..	„ 24 „	25·4	48·6	55·0
3 volumes 85% strength	12 hrs.	19·5	50·7	65·3
Further 3 volumes ..	Further 12 hrs.	17·5	51·0	68·9
	„ 42 „	18·0	51·2	68·0
3 volumes 90% strength	12 hrs.	17·5	53·8	86·6
	Further 48 hrs.	2·1	54·2	96·3
	„ 24 „	3·5	54·3	93·8
3 volumes 98% „ ..	12 hrs.	0·0	58·1	100·0

From this it will be seen that it is necessary to employ acid of about 90·0% strength in order to remove the olefines really effectively. Assuming that the figures obtained with 90 per cent. acid are correct, and that no aromatics had been removed along with the unsaturated (which is very doubtful) then aromatics are responsible for the lowering of the aniline point to the extent of 3·9°C, which, according to the relationship between aniline cloud test and aromatic content, published in the table in the Institution of Petroleum Technologists Journal, December 1922, corresponds to an aromatic content of 4·7 per cent. At this point it was decided to use an alternative method of checking, and a method which the writers think is preferable to processes involving measurement of the shrinkage of volume after various concentration of acids are employed. The method used is to decide the effect of olefines on the aniline cloud test, *i.e.*, to obtain a factor representing the amount of increase in aniline cloud point brought about by removal of a known amount of olefines. As the washes with high concentrations of acid might probably result in the removal of some of the aromatics, it is advisable to obtain this factor from the results of washes in which the removal of olefines has not been complete, but in which comparatively dilute acid has been employed, eliminating as much as possible the risk of simultaneous removal of aromatics. Therefore the factor was calculated from the results of the 80 per cent. washes. From this it will be observed that a reduction of 31 in the iodine value corresponds to an increase of 5·3°C in the aniline cloud test. As the reduction of the iodine value corresponds to the removal of 13·4% unsaturateds, we obtain the factor that one degree variation in the aniline cloud test corresponds to 2·59 per cent. in unsaturated content. Employing this factor we find that the 24·9 per cent. of

unsaturated compounds present in spirit should be responsible for 9·6°C difference in the aniline cloud test. Therefore, as the total difference in the aniline cloud test obtained by washing with 98 per cent. acid was found to be 14·7°C, the aromatic compounds should be responsible for 14·7°C—9·6°C=5·1°C, which is equivalent to 5·8 per cent. aromatic content. If this latter figure is correct, and the authors think that it is more probably correct than the direct method employing the 90 per cent. acid wash, it would mean that 90 per cent. acid has removed 1·1 per cent. of aromatics as well as effected almost completely the removal of unsaturateds. It will be noticed that the concentration of acid is quite different from the concentration advised by other experimenters, but probably 80 per cent. acid which is generally advocated as the correct concentration of effect removal of unsaturateds may be sufficient in straight run spirit, but it is not effective when cracked or other highly unsaturated spirits are under examination. By two different methods of aromatic determination, we therefore obtain figures of 4·7 and 5·8 as aromatic content. It was decided, therefore, to check these experiments by separating the various fractions and making the estimation on each fraction independently, as it was hoped thereby to obtain a check on the previous results which had been determined on a spirit in the unfractionated condition. The fractions chosen were those given in the previous mentioned list, namely boiling up to 95°C, 95°–122°C, 122°–150°C. and over 150°C. These fractions were each examined according to the method employed for the entire spirit. The results obtained were then added together, when the following figures were obtained, the values obtained from the unfractionated spirit, by two different methods, being also shown for purposes of comparison.

	By analysis of whole spirit.		By analysis of fractions.
	First method.	Second method.	
	%	%	%
Unsaturateds	24·9	24·9	.. 22·5
Naphthenes	47·7	47·7	.. 50·0
Aromatics	4·7	5·8	.. 6·8
Paraffins	22·7	21·6	.. 19·6

It is interesting to note that in the examination of the separate fractions the percentage of unsaturateds decreases as the boiling point of the product increases. For example, the benzene fraction (up to 95° C.) contained 32.5 per cent. unsaturateds; The toluene fraction (95°-122° C.) contained 22.8 per cent. unsaturateds; the xylene fraction (122°-150° C.) contained 19.9 per cent unsaturateds and the fraction over 150° C. contained 15.1 per cent. unsaturateds. The aromatic content increases with increase in the boiling point of

the fraction, *e.g.*, 5 per cent. aromatics were found in the benzene and toluene fractions, 6.7 per cent. in the xylene fraction and 12.5 per cent. in the heavier fraction. The effect on the unsaturated content is what would be anticipated, as in the cracking of a comparatively narrow fraction such as kerosene, it is probably the higher boiling constituents which undergo the cracking reaction and therefore become the lighter portions of the cracked spirit. Some of the lighter portions of the initial product (kerosene) will pass through the plant without being effected by the cracking reaction and will form the heavier portions of the cracked spirit, hence the high unsaturated content of the lower boiling fractions and comparatively low unsaturated content of the higher boiling fractions. This spirit has been tested on a variable compression engine and found to withstand detonation to a remarkable degree, its highest useful compression ratio being 5.78:1. The investigation is mainly of interest as showing the method of estimating unsaturateds by employing a factor showing their connection with the aniline cloud test.

Rumanian Light Benzine when tested by this system gave the following results.

Sp. gr.	0·730 @ 15° C.
Engler Distillation (I.P.T.)—	
Initial boiling point	= 43° C.
	1·0% @ 60° C.
	4·0% @ 70° C.
	8·0% @ 75° C.
	17·5% @ 80° C.
	39·0% @ 90° C.
	60·0% @ 100° C.
	76·5% @ 110° C.
	86·0% @ 120° C.
	89·5% @ 125° C.
	92·0% @ 130° C.
	95·0% @ 140° C.
Final boiling point	= 150° C.
Total Distillate	=97·5%
Composition of Hydrocarbons—	
Naphthenes	38·6%
Paraffins (by difference)	53·2%
Aromatics	4·2%
Unsaturateds (by calculation from iodine value)	4·0%
Unsaturateds (calculated from aniline cloud point using factor)	4·1%

It will be noted that this method gives entirely different results from those obtained by Ormandy and Craven in their paper read before the Institution of Petroleum Technologists, 10th November, 1925.

Ormandy and Craven find considerable disparity between the unsaturateds calculated by the bromine test and those found by the shrinkage in volume after 80 per cent. acid treatment. They,

however, accept shrinkage in volume as against the calculations based on the bromine value. In this point the writers disagree with them. Ormandy and Craven by estimating the aromatic content by aniline cloud test and then subtracting the aromatic content thus obtained from the total loss in 98 per cent. acid, obtain a result which closely agrees with the shrinkage brought about by 80 per cent. acid. The authors' experiments would lead them to expect this, but they believe that in both cases the results of Ormandy and Craven are far too low and that the same error has entered into the estimation by both their methods—1A and 1B. Ormandy and Craven have assumed that 80 per cent. acid gave a fairly thorough extraction of unsaturateds. The writers' experiments indicate that under the conditions used by Ormandy and Craven only approximately 32.5 per cent. of the unsaturated, would be extracted. Therefore one would expect results from Method 1A and also 1B would come to roughly one-third of the results obtained by direct calculation from the bromine or iodine number. In the spirit containing the highest estimated content of unsaturateds, namely B, the results obtained by the two methods are roughly one-third of the results obtained by direct calculation from the bromine value. There is a probability that the results obtained by calculation from the bromine value would be slightly higher than the actual unsaturated content as it is probable that a certain amount of diolefines were present and these by absorbing double the normal amount of bromine would make the figures based on the bromine or iodine value to read somewhat higher than the correct unsaturated content.

In the method 1A the aromatics are determined by the effect on the aniline cloud test, but it must be borne in mind that unsaturateds also effect the aniline cloud test and that by incomplete removal of the unsaturateds the effect of unsaturateds on the aniline cloud test has been considered as an effect of aromatics.

The writers' experiments have led them to the conclusion that a concentration of between 88 per cent. and 90 per cent. is essential for the removal of unsaturateds and that the use of 80 per cent. acid has only been continued because the majority of experimenters have been working on spirits of comparatively low unsaturated content and therefore that the effect by this incomplete removal of the unsaturateds has not been very noticeable in the results.

In conclusion the writers beg to thank the Medway Oil & Storage Co., Ltd. for the permission to publish this investigation which was carried out on their behalf.

STUDENTS' SECTION.

At a meeting of the London Branch of the Students' Section of the Institution of Petroleum Technologists on October 27, 1925, a paper on "The Economics of Petroleum" was read by Mr. J. B. Kay.

Under the heading of Production the author dealt particularly with the United States, and stated that in 1920 258,600 wells and in 1924 350,000 wells were producing oil. In 1913 the total number of wells drilled was 26,000, and in 1924 30,000, and 30,000 new wells were responsible for 400 million barrels of oil per annum.

The world's annual consumption of oil in 1924 was 1000 million barrels, and is estimated to be double that quantity by 1929. While improved extraction methods make for larger production, they also mean speedier depletion.

The average cost of drilling to a depth of 1500 feet is £3500 to £5000, and to 5000 feet, £20,000 to £50,000.

Over 50,000 miles of pipe-lines are in use in the United States, and laying costs average from £2000 to £5000 per mile.

The average percentages of products extracted from crude oil during 1924 were: Gasoline, 30·0; Kerosene, 12·4; Gas and Fuel Oils, 46·6; Lubricating Oils, 4·0; the figures for 1917 being 21·2, 12·8, 48·4 and 5·6 respectively. Since 1914 the prices of gasoline have been comparatively stable, while other products have increased in price.

A joint paper by Messrs. H. R. Lovely and F. P. C. Feilman on "Some Polish Experiences" was read before the London Branch, Students' Section of the Institution of Petroleum Technologists, by Mr. Feilman on November 17.

In July, 1925, the writers of the paper spent some time studying oilfield geology in the Galician oilfields. They refer to the occurrence of overthrusts which have caused strata of Cretaceous, Eocene and Oligocene age to be thrust forward over the Miocene (Salifere) in the Carpathian foot-hills. They also remark on the scarcity of fossils and reliable index beds, and they carried out some heavy mineral examinations of two sandstones, the Wygoda of Eocene age and the Jamna of Eocene-Cretaceous age. The

results of these tests on a limited number of samples in a restricted area indicated differences that might enable the two somewhat similar beds to be distinguished. Whilst both sandstones contain the minerals Ilmanite, Tourmaline, Zircon, Garnet, Rutile and Staurolite, the Wygoda contains in addition Kyanite, which is absent in the Jamna, and the Jamna includes Epidote, absent in the Wygoda.

REVIEWS.

ÉLÉMENTS DE LA TECHNIQUE DU PÉTROLE. By Georges Lévi. 100 pp. Paris, 1925.

ALTHOUGH the writer states in his preface that this small book contains only an outline of the subject, sufficient to give a technical class an insight into the same, one is struck by the completeness of the summary. The author ranges over the whole subject of Petroleum Production Technology, if sometimes in the briefest manner, but always touching the most salient points. One realises the interest that is taken in France in regard to a National Petroleum Industry in reading M. Pineau's preface to the book.

M. Lévi has subdivided his subject in a clear and logical manner, as can be observed from the table he gives on page 14. This naturally falls, in the usual way, into the two main groups of Percussion and Rotary Drilling methods. The former is then subdivided into those methods employing rigid and flexible means of suspension (rods and ropes), and the further subdivision falls into methods of continuous and interrupted cleaning of the well (the one by flush and the other by bailing).

He thus considers each of the following systems as it falls into one or other of the above groups and subdivisions: Canadian, Fauvelle, Raky and cable, with and without continuous flush. Under the Rotary group he deals with the hand Auger, the flush Rotary and the Diamond, Calyx and Shot methods. The first part of his book deals with the subject as outlined above. The second part is devoted to what is the main feature of the Pechelbronn field, the exploitation of oil by means of pits and galleries.

M. Lévi deals theoretically with the methods of recovery of oil from oil sands. It is, of course, well known that by to-day's production methods only about 20 per cent. of the oil is recoverable. This the author correctly points out. He suggests that the remainder may be recoverable as to 40 per cent. by means of subterranean galleries (on the Pechelbronn system presumably), and the remaining 40 per cent. by the wholesale extraction of the oil bearing rock and the recovery of the oil from the latter by treatment with warm water. In describing the last two recovery methods as only applicable in certain cases, he regards the matter from a practical point of view, as it is hardly possible that such methods of recovery can be applicable generally on oilfields. In exhausted shallow fields, such as Campina, Roumania, the second method is, however, now being tried, and the results being watched with much interest.

Since writing the above, attention may be drawn to the most interesting and instructive paper by Leo Ranney, read on November 20 before the joint session of the American Institute of Mechanical Engineers and the American Society of Mining and Metallurgy. According to the author of this paper, great depth is not necessarily a hindrance to this process of recovery of oil by means of shafts.

The different tools employed in drilling are briefly explained with marginal sketches. One notices the absence of any description of under-reaming methods, either by means of one or other of the specialised tools for that purpose, or even of the eccentric bit used in the Galician drilling system.

One questions, somewhat, the sizes of drilling rods given on page 11, where dimensions of from 25 mm. to 100 mm. are given. The usual pole size is the former. The heaviest rods in the Russian system were 1¼ in. or about

40 mm. Anything above this must be regarded as a size for special purposes, as for fishing, and not for ordinary drilling.

A good description is given of the relative functions of the jars and freefall, and the author correctly points out the advantage of the latter in lessening the shock on the rods in lifting the tools at the moment of zero speed, whereas the jars effect this at the point of maximum speed. So far as the compressive stresses on the rods are concerned, these are absorbed in both systems.

With regard to the author's remarks on Casing (p. 34), one does not see why an average well to-day proceeding to a depth of 1000 metres should require an initial diameter of one metre (nearly 40 in.) as stated. Such initial diameters were used in some cases formerly on the Russian oilfields where the conditions were special, but which to-day are gradually changing. Nor is there any reason why in the water shut off sections given on page 34, the well, with all casing left intact, should be more watertight than the one with the upper portions of the casing cut out and recovered. Watertightness in such cases depends primarily on the setting of the shoe, and the tightness of the casing, which, in the two cases shown, are presumably identical.

Cementation and water shut off methods are necessarily dealt with very briefly.

The author gives a short summary on page 55 of the different drilling methods in use, grouping this under the heads of :—

1. Percussion System with Rods;
2. Rapid Blow Percussion System;
3. Cable System, and
4. Coring Method and Rotary Drilling.

One might suggest that rather too much is made of the first method, which, for the deeper drilling of the present day, is, by reason of its mechanical deficiencies, being rapidly superseded by the other systems described.

The author touches on the question whether water flush methods are entirely satisfactory for exploratory work. His opinion appears to be not unfavourable, provided proper safeguards are adopted. This is a debatable matter upon which opinions still vary considerably.

The difficulties with regard to proper well spacing are alluded to, and the author points out how almost impossible it is to formulate precise rules on this matter. One might point out the results recently arrived at by the U.S. Bureau of Mines, which show that over-spacing decreases the amount of oil recoverable, while under-spacing may cause financial loss, as, although a greater ultimate production per well may be obtained, the production per acre of the area may be much less than with more closely spaced wells.

The above notes will indicate the wide range covered by this booklet in a condensed form in discussing the more prevalent exploration and exploitation methods of the present day.

The second part, dealing with exploitation by means of pits and galleries, is an interesting summary of a method which is directing attention to itself to-day as a possible means of increasing the recovery from oil sands, at any rate from shallower depths. This part, read in conjunction with M. P. de Chambrier's recent paper, read before the Institution of Petroleum Technologists, will give a good exposition of the subject.

F. G. R.

ACCOUNTING FOR THE PETROLEUM INDUSTRY. By D. F. Morland and R. W. McKee. McGraw Hill. £1.

In this work the authors presume a thorough knowledge of accountancy by their readers. It is designed to present a general system of accounting

applicable to the Oil Industry, and couples with it an extensive card record system which, while it is separate from the accounts, is based thereon, and is so arranged that almost any information required by the management is available at a moment's notice. At the same time a caution is sounded against too minute a classification which involves unnecessary labour.

The system advocated is based on American practice, where, partly in view of the elaborate form of taxation, the science of accountancy and the preparation of statistics has been the subject of exceptional study and receives particular attention, which fact is reflected in the large powers and high salary of "the Controller," as the principal accountant of a Corporation is called in the U.S.A. The principles enunciated, however, can be equally well applied to any country in which operations are conducted.

The subject is discussed in clear and simple language under the following sections: Production; Transportation and Storage; Refining; Marketing, and the all-important matter of United States Federal Taxation.

Each section deals with complete accounting for the particular branch under review—facilitating quick reference—while the work covers the whole field of accounting for the Petroleum Industry.

A useful feature is the opening of each section with a description on broad lines of the procedure and technology of the branch of the industry being handled, which should enable the accountant to accumulate a sufficient knowledge to grasp what is required of him. Each phase of the particular section is then dealt with in proper sequence, and the section is concluded with a chapter devoted to the classification of the accounts and records used, followed by a tabulated list and numerous specimen rulings.

Due regard is shown to mould the accounts in such manner as to involve the minimum liability for income tax, and conservative finance is advocated.

No hard and fast rules are (or could be) laid down, and in some instances alternative methods are discussed for application to any particular company.

Under the Refining Section costing is dealt with at some length, supported by examples.

While admitting that the subject of Federal income tax as it affects this Industry is worthy of an entire volume to itself, a very useful résumé of the subject is incorporated. The difficult problem of depletion is referred to both in this section and in a separate chapter devoted to it in the Production Section. The authors wisely state that "it has truthfully been said that income taxes are composed of about one point of law and nine points of accounting. It may be mentioned that taxation procedure . . . . is much too technical to be left wholly in the hands of either an accountant, a petroleum engineer, or a lawyer," and then describe the proper functions of each of these specialists, enlarging on the work falling to the lot of the accountant. No reference, however, is made to certain principles which apply to companies registered outside the U.S.A.

Without going into great detail, the authors have touched on practically all phases of the business in any way connected with a large accounting staff of a company interested in the Industry, from the acquisition of the property to the retail selling of the finished products, and a complete system could be modelled from a study of the volume. H. T.

PRINCIPLES AND PRACTICE OF INDUSTRIAL DISTILLATION. By E. Hausbrand. Translated by E. H. Tripp. London: Chapman and Hall. 21s. net.

Hausbrand's work has so long been recognised as authoritative in its country of origin that it is strange that it was not translated long ago. In a sense it may be said that Hausbrand to the commercial distiller plays somewhat the same rôle as does Young in the laboratory. The work is

literally indispensable to designers of fractionating apparatus, although it does not attempt in any way to deal with the constructional side of such apparatus. The work is divided into four parts, the first of which deals with the theory of the plant in necessarily cumbersome mathematical form. The second part deals with the application of the calculations in part 1 as applied to a number of specific examples, such as fractionating of ethyl alcohol and water, methyl alcohol and water, acetone and water, acetone and methyl alcohol, methyl alcohol and ethyl alcohol, acetic and water, formic acid and water and ammonia and water, together with the separation of the constituents of air, and of water and nitric acid. Part 3 is devoted to tables and part 4 to charts. The much debated problem of the correct temperature of the reflux condenser is dealt with, and there is little doubt that the Industry as a whole agrees with the decision at which Hausbrand arrives, and this applies also to the question of the proper point of delivery of the reflux into the column. As regards the translation, it is impossible to say more than that the work is so well done that very few people would ever realise that it was a translation, and in dealing with such technical matters this is high praise. W. R. O.

LUBRICATING OILS, FATS AND GREASES. By George H. Hurst. 4th Edition, revised by H. B. Stocks. London: Scott, Greenwood and Son. 12s. 6d. net.

This book, which was originally produced in 1896, has been brought up fairly well to date, and now contains much condensed information in its four hundred pages, which was only available hitherto in a scattered form in the literature. The scope of the volume is wide, and therefore very detailed information is not to be expected under all the headings. The hope "that the present work may be of interest and use to those engaged in the manufacture of lubricants, etc.," expressed in the concluding paragraph of the preface, appears to be justified.

The introductions to the general chemistry of the hydrocarbon oils, and to the vegetable and animal oils and fats, constitute a brief recapitulation useful to readers having some knowledge of organic chemistry. The refining of Scotch shale oils and the methods of extraction, and properties of the vegetable and animal oils and fats, are dealt with in some detail. Some fifty pages are devoted to the petroleum oils and their distillation for the production of lubricants. The refining or finishing of the lubricating oil fractions is dealt with rather briefly. The section devoted to lubricating greases contains a considerable amount of valuable information and a number of useful recipes.

The "internal explosion engine," its lubrication, and the characteristics of suitable oils are discussed. In this section a brief reference to the recent work in the dilution of automobile crank-case lubricating oils, and the characteristics of used and reclaimed oils, might well have been included.

In the section devoted to friction the laws of friction are given, and the modern conception of the cause of oiliness is indicated. The views and experimental work of Archbutt, Deeley, Dunstan and Thole, Hardy, Mabery, Wells and Southcombe and others are mentioned.

The chapter on the analysis and testing of oils includes the more usual physical and chemical tests, descriptions of various standard viscometers, and of methods of determining absolute viscosity. A definition of absolute viscosity might well have been included. Various testing machines, such as that of Thurstin, are described, and the results obtained under boundary condition of lubrication in the Lanchester Worm Gear Testing Machine and Deeley's Machine are also included. R. W. L. C.

BOOKS RECEIVED.

REPORT OF THE FUEL RESEARCH BOARD FOR THE PERIOD ENDED DECEMBER 31ST, 1924. London: H.M. Stationery Office, 1925. 1s. 6d. net.

This report contains also the Report of the Director of Fuel Research. The last general report was published early in 1920, and the present work deals with the work carried out at the Fuel Research Station at East Greenwich in connection with the National Coal Resources, the Gas Industry, Low Temperature Carbonisation, Steam Raising, Internal Combustion Engines, Power Alcohol, Peat, etc.

THE LANCASHIRE COALFIELD: THE SMITH SEAM. London: H.M. Stationery Office, 1925. 1s. 6d. net.

This is No. 5 of the Physical and Chemical Survey of the National Coal Resources Series, published by the Fuel Research Board, and describes laboratory experiments carried out by the Lancashire and Cheshire Coal Research Association.

SCOTTISH SHALE INDUSTRY. London: H.M. Stationery Office, 1925. 3d. net.

Is the report by the accountants appointed by the Board of Trade on the costs of Production and Financial Results in the Shale Industry carried on by Scottish Oils, Ltd., and its Associated Undertakings.

ANALYSIS OF ALBERTA COAL. Scientific and Industrial Research Council of Alberta, 1925. 25 cents.

Contains figures based on analyses of 464 samples of Alberta coals arranged in areas and districts. In each case a typical analysis is given, and maximum and minimum values to indicate the range of variations. Maps and charts are also included to indicate the location of the various districts.

A BIBLIOGRAPHY OF BIBLIOGRAPHIES ON CHEMISTRY AND CHEMICAL TECHNOLOGY, 1900-1924. By Clarence J. West and D. D. Berolzeimer. National Research Council, Washington, D.C., Bulletin No. 50. 308 pp. $2·50.

This work is composed of the following sections: General Bibliographies, Abstract Journals and Year-Books, General Indexes of Serials, Bibliographies of Special Subjects and Personal Bibliographies. As the title indicates, the work is a compilation of bibliographies published as separates, or at the end of books or magazine articles, or as footnotes to the same, on the numerous aspects of pure and applied chemistry. Each entry gives name of author or compiler, title and place of publication. The majority of the entries state the number of references, thus giving an indication of the completeness of the particular bibliography. The entries are classified under the proper subject-headings, alphabetically arranged. The duplication of individual entries has been largely avoided by the liberal use of cross-references. An approximate analysis shows that there are about 2400 subject headings, 7500 author entries, and a total of 10,000 individual bibliographies.

CURRENT PETROLEUM NOTES.

PRINCE EDWARD ISLAND.—According to a bulletin received from the High Commissioner for Canada in London, Mr. Ross M. Stuntz, manager-in-charge of field operations, has announced the Henry L. Doherty Company of New York have completed plans for the commencement of their drilling programme in Prince Edward Island. Mr. Stuntz stated that his personal opinion was that, should oil in commercial quantities be discovered in the Maritime Provinces, it would be refined and marketed there, and that only amounts in excess of such local requirements would be exported. The company hoped to start drilling about November 1st, 1925.

CANADA.—The following is extracted from an article by Dr. Charles Camsell, Deputy Minister of Mines, contained in the Canadian Official Mining News Letter (No. 67) received from the High Commissioner for Canada in London :—

One of the interesting features of mining development in Canada is the new outlook for oil production in Alberta as a result of developments in Turner Valley in the foothills region. Up to last year the energies of oil mining companies had been devoted almost entirely to the search for oil in strata near the base of the Cretaceous formations. The finding of a heavy flow of wet gas far below this horizon in Carboniferous strata last year has presented new possibilities and given a fresh impetus to oil prospecting. Attention is consequently being directed to deeper drilling in the foothills belt, where structures are more pronounced and more easily detected than in the plains.

The particular well responsible for the optimism which prevails struck a heavy blow of gas last year at 3740 ft. The gas is under such pressure that as a result of expansion it reaches the cellar of the well at a temperature of 22° (F.) below zero. The well was out of control for a short time, but for some months past a daily recovery of about 500 barrels of gasoline has been made from the gas.

ALBERTA.—The High Commissioner for Canada in London has received from the Dominion Department of Mines the following article (Canadian Official Mining News Letter, No. 71), prepared by Dr. G. S. Hume, of the Geological Survey Branch, dealing with Oil Development in Alberta :—

Prospects for the development of a large production of oil in Alberta have never appeared more promising than now. This

expectation is based upon geological conditions and present production in the Turner Valley field, south-west of Calgary, and in the Wainwright field, 120 miles east of Edmonton.

British Petroleums, Limited, first struck oil in their well No. 2 at Wainwright late in 1923, and again in 1924 in their No. 4 well. Their No. 3 well, drilled to a deeper horizon, was abandoned because of production troubles, but this year a well drilled close to No. 3 has been producing satisfactorily. This well, known as No. 3A, is yielding oil of much better quality than the others, and no production troubles are anticipated.

A geological study of the Wainwright structure would indicate possibilities of greater production from these deeper horizons, and if other wells were drilled in another part of the structure where the same degree of oil saturation exists in the deeper sand as at No. 3 well, much greater production might reasonably be expected. From the information now available the best location for a test would be close to British Petroleums No. 2 and No. 4 wells, and it is understood that such a test has already been contemplated by a company interested in the Wainwright field.

A small quantity of light oil has been produced by the Turner Valley or Sheep River field for several years, and development was stimulated by the discovery late in 1924 of a tremendous flow of wet gas in the Royalite Company's No. 4 well at a depth of 3740 ft. The well cannot be completely shut in because of the tremendous pressure, and the gas is therefore allowed to flow at the rate of 17,000,000 cub. ft. a day. Two separators have been erected on the pipe line to extract gasoline from the gas, and during the first six months of 1925 the well produced 423 barrels of gasoline a day. Production for May and August from No. 4 exceeded its monthly average from January to April. The oil and gas both contain hydrogen sulphite. The gasoline is treated in the Imperial Oil refinery at Calgary, and a scrubbing plant to treat the gas is under consideration.

Several other wells are now being sunk in this field. The Royalite Company is drilling two more, No. 5 and No. 6. No. 5 is slightly to the north of No. 4, and the latest information from the Imperial Oil Company gives its depth as 1152 ft., with a 12½ in. casing set at 1544 ft. No. 6 is down about 1466 ft. with a 12½ in. casing set at 1224. A show of oil and gas was obtained from the latter at 1330 ft. In addition, good progress is being made by the Vulcan and the McLeod Oil Companies, and drilling is proceeding at several other leases. The discovery of oil at the Royalite well has given a great impetus to the search for other favourite locations, and a great deal of exploratory work will doubtless be done very soon.

Tests are being made in other parts of the province. At Medicine Hat the Roth well is being drilled, and the Medicine Hat-Redcliffe area has produced a large amount of gas for industrial and domestic use. Much drilling has been done in southern Alberta following the discovery of oil a few years ago in the Kevin-Sunburst field of Montana close to the international boundary, but no commercial products have yet been found. The Imperial Oil Company is drilling a test well south of Turner Valley at Rice Creek, and another at Coalspur in the north, but neither of these tests has yet been completed.